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ON THE

PROGRESS OF CHEMISTRY

FOR 1911.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
A.	Abstracts in Journal of the Chemical Society.*
Amer. Chem. J.	American Chemical Journal.
Amer. J. Physiol	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Falsif.	Annales des Falsifications.
Ann. of Botany	Annals of Botany.
Ann. Physik	Annalen der Physik.
Ann. Report	Annual Reports of the Chemical Society.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy
Arch. expt. Path. Pharm.	Archiv. für experimentelle Pathologie und Pharmakologie.
Arch. Néerland	Archives Néelandaises des sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Boll. chim. farm.	Bollettino chimico farmaceutico.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci., St. Pétersbourg	Bulletin de l'Academie Impériale des Sciences de St. Pétersbourg.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. géol. Belgique	Bulletin de la Société géologique de Belgique.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Föld. Közlöny	Földtani Közlöny.
Gazzetta	Gazzetta chimica italiana.
Gummi-Zeit.	Gummi-Zeitung.
J. Agric. Sci.	Journal of Agricultural Science.

* The year is not inserted in references to 1911.

Abbreviated Title.	Journal.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
Jahrb. Radioaktiv. Elektronik	Jahrbuch der Radioaktivität und Elektronik.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Mem. Coll. Sci. Eng., Kyōtō	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Mon. sci.	Moniteur scientifique.
Österr. Zeitsch. Berg. Hüttenwesen	Österreichische Zeitschrift für Berg- und Hüttenwesen.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Proc.	Proceedings of the Chemical Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. London Phys. Soc.	Proceedings of the London Physical Society.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. Micro-Science	Quarterly Journal of Microscopic Science.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli	Rendiconto dell' Accademia delle Sienze Fisiche e Matematiche-Napoli.
Rev. gén. Chim. pure appl.	Revue générale de Chimie pure et appliquée.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Trans.	Transactions of the Chemical Society.
Trans. Eng. Ceramic Soc.	Transactions of the English Ceramic Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.

Abbreviated Title.	Journal.
Zeitsch. Biol. . . .	Zeitschrift für Biologie.
Zeitsch. Chem. Ind. Kolloide.	Zeitschrift für Chemie und Industrie der Kolloide.
Zeitsch. Elektrochem. . .	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min. . .	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genussm .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl. Chem. .	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem. .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem. .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zentr. Physiol. . . .	Zentralblatt für Physiologie.

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GENERAL AND PHYSICAL CHEMISTRY.

In the report which follows, no attempt has been made to summarise the whole of the work accomplished during the year. It has been thought preferable, as in previous years, to select for review a limited number of topics in which marked advances have been made, and to hold over for subsequent discussion other branches of work in which important investigations are still in progress.

The Properties of Water.

During the past year some of the fundamental properties of water have been redetermined. W. R. and W. E. Bousfield[1] have determined the *heat capacity in absolute units*, over the range from 13° to 55°, to be 4·182 joules per gram-degree Centigrade, as compared with the figure 4·175 given by Barnes; for the heat capacity at 15° they give the value 4·179 as compared with the figure 4·184 of Barnes; but nearly all observers agree in giving the value 4·174 for the heat capacity at 30°.

The heat capacity of water varies considerably with temperature, and possesses the almost unique property of passing through a minimum; this is now given at 25°, the variation of the heat-capacity J with temperature θ being expressed by the formula:

$$J = 4{\cdot}2085 - 0{\cdot}003022\theta + 0{\cdot}00007833\theta^2 - 0{\cdot}0000004900\theta^3.$$

Taking the 15° calorie as unity, the *specific heat* at other temperatures is given as follows:

θ =	0°	10°	20°	30°	40°	50°	60°	70°	80°
J =	1·0070	1·0016	0·9991	0·9990	1·0006	1·0031	1·0058	1·0080	1·0091
J =	1·0067 (0°)		0·9994 (20°)		1·005 (35°)		(A. Cotty.)		

The three values given in the lower line are those obtained by

[1] *Phil. Trans.*, 1911, A, **211**, 199; *A.*, ii, 580.

A. Cotty[2] in a series of measurements made with the help of a Bunsen calorimeter. The close agreement between the values given by different observers for the variations of specific heat below 20° does not appear at higher temperatures, recent values for the specific heat at 80° ranging over no less than 1 per cent.

In connexion with an investigation of the refractive indices of salt solutions, the *refractive index* of water has been measured at 20°, 25°, and 30° by G. P. Baxter, L. L. Burgess, and H. W. Daudt.[3] Their values of $[n]_D$ are:

20°	1·33299 in air	1·33335 in a vacuum
25°	1·33248 ,,	1·33284 ,,
30°	1·33190 ,,	1·33225 ,,

In the case of electric waves from 3·5 to 4·5 cm. long, water has been shown to exhibit anomalous dispersion, the refractive index increasing instead of diminishing with increasing wave-length.[4]

The Boiling of Water.

The phenomena attending the boiling of water have been investigated by the Earl of Berkeley and M. P. Applebey,[5] with special reference to the considerable variations of temperature that appear when the rate of boiling, or the height of the column of liquid through which the steam has to pass, is changed. The temperature-measurements were made differentially with the help of two platinum-resistance thermometers, one immersed in the steam of an ordinary hypsometer, and the other in a steam-jacketed tube, in which water was boiled by the passage of steam from the enclosing wide-necked flask. In a typical series of observations, the excess of temperature of the water in the tube was 0·0481° when distilling 1·2 c.c. of water in ten minutes, diminishing to 0·0243° when distilling 32·8 c.c. The temperature of the boiling liquid was raised from 0·0384° above the hypsometer-temperature to 0·0620° above, when the height of liquid was increased from 5·5 to 7·8 cm., in spite of a small increase in the rate of distillation; under similar conditions, a tube 5·75 cm. in diameter gave readings 0·008° lower than a tube 4·4 cm. in diameter. It is shown that the excess of temperature is given by the equation:

$$t = kah^2/(h+\beta),$$

where h is the height of liquid, k a constant, and a and β are quantities depending on the rate of bubbling. The importance of

[2] *Ann. Chim. Phys.*, 1911, [viii], **24**, 282; *A.*, ii, 964.
[3] *J. Amer. Chem. Soc.*, 1911, **33**, 893; *A.*, ii, 557.
[4] H. Merczyng, *Bull. Acad. Sci. Cracow*, 1911, 123; *A.*, ii, 574.
[5] *Proc. Roy. Soc.*, 1911, **A, 85**, 477; *A.*, ii, 1061.

this equation depends on the fact that the hypsometer-temperatures cannot be measured in the case of solutions, the boiling points of which must therefore be seriously in error when measured in the ordinary way without correction; it is perhaps for this reason that the cryoscopic method has usually been preferred for determinations of molecular weight.

Boiling Points of Saturated Solutions.

Using the corrections as worked out for pure water, the boiling points of a series of saturated solutions, reduced to standard conditions, were found [6] to be as follows:

Salt.	Boiling point.	Osmotic pressure, atmos.	No. of gram-mols. per litre of solution.	Osmotic pressure / Gram-mols. per litre
NaCl	108·668	476·8	5·648	84·4
KCl	108·599	473·3	5·985	79·1
RbCl.....	113·510	743·2	7·948	93·5
CsCl	119·919	1055 0	9·214	114·5
TlCl	100·097	5·5	0·097	57·0
Na_2SO_4.....	102·885	162·2	2 596	62·5
K_2SO_4	101·392	79·4	1·255	63·2
Rb_2SO_4	103·511	197·0	2·505	78·6
Cs_2SO_4	109·963	545 4	4·015	135·8
Tl_2SO_4	100·317	17·8	0·347	51·3
$NaNO_3$.....	120·20	1062 9	12·276	86·6
KNO_3	115·549	838·3	12·756	65·7
$RbNO_3$.....	119·4	1041·0	12·828	81·2
$CsNO_3$	107·228	398·1	6·617	60·2
$TlNO_3$	104·7	264·0	11·058	23·9
$Sr(NO_3)_2$	106·790	376·2	3·588	104·8
Cæsium alum ...	100·527	21·2	0·300	70·1

The table shows also the osmotic pressure as calculated from the boiling points by means of a modified form of Porter's equation.

Determination of Boiling Points.

A method of determining boiling points accurately with minute quantities (0·03 to 0·1 gram) of a substance is described by A. Smith and A. W. C. Menzies.[7] The liquid is contained in a bulb with a capillary opening turned downwards; the bulb is attached to a thermometer suspended in a beaker filled with calcium chloride solution, sulphuric acid, paraffin, or fusible nitrates; this bath is heated until the boiling liquid has been freed from gases, and pure vapour is being driven out; the boiling point is the temperature at which bubbles cease to form when the well-stirred bath is allowed to cool. If the liquid is soluble in the bath, the temperature is

[6] *Proc. Roy. Soc.*, 1911, A, **85**, 489; *A.*, ii, 1062.

[7] *J. Amer. Chem. Soc.*, 1910, **32**, 897; *Proc. Roy. Soc. Edin.*, 1910, **30**, 432; *A.*, 1910, ii, 687.

allowed to fall until the bath-liquid has risen 5 to 10 mm. in the capillary tube. A correction is needed for the "head" of bath-liquid through which the vapour has to be driven; this must be read to 2 mm. The corrected boiling points are usually within a few hundredths of those determined in the ordinary way with large quantities of liquids. The method can be applied to non-fusing solids, such as calomel and ammonium carbonate. By placing the submerged bulblet and the thermometer inside a test-tube containing some of the bath-liquid, instead of directly in the open bath, the pressure at which the boiling point is determined can be varied.[8] In this form the method is specially applicable to the determination of boiling points at 760 mm. exactly instead of at the arbitrary and variable pressure of the atmosphere. The method can also be applied to the measurement of vapour pressures over a range of temperatures. For reducing boiling points measured at pressures near 760 mm., the following rule is given: *Divide* 8500 *by the boiling point on the absolute scale, and the quotient is the change of pressure in mm. for* 1° *change of boiling point*[9]; the values calculated by this rule are usually correct within 1 mm., but for water and other hydroxylated liquids the constant 10,200 must be used. Attention is directed[10] to the fact that boiling points at low pressures are usually 0·10° to 0·17° too low, owing to the expansion of the bulb of the thermometer on the removal of the atmospheric pressure. At high pressures the reduction of the barometric height to mm. of mercury at 0° and to 45° latitude at sea-level are equally important; the latter correction amounts to 0·25 mm. per atmosphere at Chicago and 0·5 mm. per atmosphere in London.[11]

The Measurement of Vapour Pressures.

In a critical review of the methods used in determining vapour pressures, A. Smith and A. W. C. Menzies[12] point out that the static method (for example, introducing the substance into the Torricellian vacuum of a jacketed barometer tube) is subject to very large errors on account of gases and other volatile impurities occluded on the walls of the barometer tube and dissolved in the liquid to be vaporised. In the dynamic method, in which the boiling point is determined at different pressures, the chief difficulty

[8] A. Smith and A. W. C. Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 907; *Proc. Roy. Soc. Edin.*, 1910, **30**, 437; *A.*, 1910, ii, 688.

[9] Compare S. Young, *Trans.*, 1902, **81**, 777.

[10] A. Smith and A. W. C. Menzies, *Proc. Roy. Soc. Edin.*, 1910, **30**, 436; *J. Amer. Chem. Soc.*, 1910, **32**, 905; *A.*, 1910, ii, 688.

[11] *J. Amer. Chem. Soc.*, 1910, **32**, 1414; *A.*, 1910, ii, 1036.

[12] *Ibid.*, 1412; *Ann. Physik*, 1910, [iv], **33**, 971; *A.*, 1910, ii, 1036.

consists in securing exact equality between the temperature of the vapour and that of the thermometer, overheating being specially frequent at low pressures and underheating at high temperatures, as, for example, in determining the boiling point of sulphur. The authors have modified their "submerged bulblet" apparatus in such a way that it can be used as a "static isoteniscope" for the measurement of vapour pressures by a static method. This has been done by adding a U-tube to the downward-pointing capillary of the bulb; this U-tube leads right out of the bath to an apparatus in which the air-pressure can be varied and measured. The U-tube is usually filled, not with mercury, but with the same liquid that is under examination in the bulb; this liquid is boiled repeatedly by suitably adjusting the pressure until quite free from air, and finally a pressure is found which leaves the liquid in the U-tube at exactly the same level in the two arms. The temperature of the violently-stirred bath was read by means of a platinum resistance thermometer.

By using this method, values were obtained for the vapour pressure of water from 50° to 90°, which differed from those of Holborn and Henning [13] by an average of only +0·08 mm. or −0·0063°; this divergence is one-tenth and one-thirtieth of that shown by the measurements of Magnus and of Batelli respectively. The actual figures are:

t =	50°	60°	70°	80°	90°
p =	92·27	149·13	233·44	354·90	525·94 (S. and M.)
p =	92·30	149·19	233·53	355·1	525·8 (H. and H.)

Reference may also be made to a series of measurements of the vapour pressure of water by F. C. Krauskopf,[14] who gives the following figures:

Temperature =	25°	30°	35°	40°	50°	60°	70°	80°
Vapour pressure =	23·71	31·84	41·91	55·18	92·16	149·26	233·99	355·08

These values, obtained by saturating a current of air with water, differ considerably from those given in the tables of Landolt and Börnstein (based mainly on the measurements of Regnault), but are in good agreement with the values given by Perman,[15] and by Holborn and Henning.

By means of their "static isoteniscope," Smith and Menzies [16] have redetermined the vapour pressures of mercury from 250° to

[13] *Ann. Physik*, 1908, [iv], **26**, 833.

[14] *J. Physical Chem.*, 1910, **14**, 489; *A.*, 1910, ii, 688.

[15] *Proc. Roy. Soc.*, 1903, **72**, 72.

[16] *J. Amer. Chem. Soc.*, 1910, **32**, 1434; *Ann Physik*, 1910, [iv], **33**, 979; *A.*, 1910, ii, 1037.

435°. Their values are extraordinarily smooth, the average deviation from those calculated from the formula:

$$\log p = 9{\cdot}9073436 - 3276{\cdot}628/\theta - 0{\cdot}6519904 \log \theta$$

being only 0·050°, as compared with 1·2° in the observations of Gebhardt, and 3·29° in those of Regnault. The boiling point at 760 mm. pressure (reduced to 0°, 45° latitude and sea-level) was found to be 356·95° ± 0·1° (thermodynamic scale); Regnault's value was 357·7°, whilst the value of Callendar and Griffiths on the same scale is 357·08°. Values calculated from the formula are given in a table for every 2° from 0° to 45°. Typical values are:

0°	50°	100°	150°	200°	250°	300°	350°	400°	450°
0·000207	0·01340	0·2793	2·811	17·22	74·10	304·69	669·77	1566·1	3245·0

A variety of the "submerged bulblet" apparatus, modified only in construction, and made entirely of glass, is described by the authors as a "dynamic isoteniscope.[17] The capillary of the small bulb is sealed into a larger bulb, 23 mm. in diameter, which contains enough of the confining liquid (usually, but not always, the same as the liquid under examination) to cover the opening of the capillary tube; this larger bulb is connected to the apparatus for regulating and measuring the pressure, the whole apparatus being immersed in a well-stirred heating bath. Measurements of the vapour pressure of benzene, with sulphuric acid as the confining liquid, between 65° and 120° gave vapour pressures appreciably higher throughout than those of Young, Regnault's values being intermediate between the two series. The boiling point at 760 mm. (corr.) was found to be 80·12°, as compared with 80·20°, the value given by Louguinine.

Vapour Pressure of Ammonium Chloride and of Calomel.

The "dynamic isoteniscope" was used to measure the vapour pressures between 280° and 333° of solid ammonium chloride, the values for which were subject to large errors on account of the difficulty of measuring the vapour pressures or boiling (sublimation) points of volatile solids. Using fused nitrates as the confining liquid, the vapour pressures were found to increase from 131 mm. at 278·3° to 633 mm. at 332·9°; the values agree closely with those obtained by Ramsay and Young[18] by a statical method in which the salt was vaporised over mercury, but differ widely from those obtained by a dynamic method in which the salt was mixed with mercury and distilled off under measured pressures at temperatures recorded by a thermometer immersed in the mercury.

[17] A. Smith and A. W. C. Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1448; *Ann. Physik*, 1910, [iv], **33**, 989; *A.*, 1910, ii, 1038. [18] *Phil. Trans.*, 1886, **177**, 71.

The vapour pressure of calomel was investigated [19] in order to ascertain the nature of the vapour, and, in particular, to find out whether it consisted mainly or not at all of undissociated calomel. It was shown that if no dissociation took place the vapour pressure of a mixture of calomel and mercury would be equal to the sum of the separate vapour pressures, whereas if dissociation were complete the mixture would give a smaller vapour pressure, namely, that of the mercury *plus* $(\frac{1}{2}P_C)^2/P_M$, where P_C = vapour pressure of calomel, P_M = vapour pressure of mercury. The experimental values were found to be even lower than those calculated for complete dissociation. This was found to be due to the solubility of calomel in mercury, to the extent, for instance, of one part of calomel in 21·3 parts of mercury at 398°. This would lower the vapour pressure of the mercury by an amount depending on the molecular weight of the calomel. Assuming, however, the calomel dissolved in mercury to have the simple formula HgCl, the vapour pressures of mixtures of calomel and mercury were found, in a series of nine observations between 360° and 400°, to give average values differing by only −0·13 mm. from those calculated for complete dissociation.

The boiling point of calomel under normal pressure is given as 382·5°.

A further investigation was made of the vapour pressure of dried calomel.[20] The bulb containing the substance was sealed to a bulb containing phosphoric oxide and to a large bulb intended for vapour density determinations. The bulb of phosphoric oxide was sealed off after five and a-half months, during which the calomel had been heated to 115°, and the oxide cooled by circulating water. The two remaining bulbs were then heated to 352° for fifteen minutes, when the larger bulb was sealed off and weighed. No calomel was found in this bulb, indicating that the vapour pressure (which would usually have been about half an atmosphere) had been reduced to zero by careful drying. Baker [21] found for dried calomel at 445° a vapour density corresponding with the formula Hg_2Cl_2 (found 435, calc. 470), whereas the undried material appeared to be completely dissociated.

[19] A. Smith and A. W. C. Menzies, *Proc. Roy. Soc. Edin.*, 1910, **31**, 183; *J. Amer. Chem. Soc.*, 1910, **32**, 1541; *A.*, ii, 114.

[20] A. Smith and A. W. C. Menzies, *Zeitsch. physikal. Chem.*, 1911, **76**, 713; *A.*, ii, 492. Compare A. Smith, *J. Amer. Chem. Soc.*, 1910, **32**, 187; *A.*, 1910, ii, 273. Also *Ann. Report*, 1908, 24.

[21] *Trans.*, 1900, **77**, 646.

Molecular Weights Deduced from Vapour Pressures.

An instrument somewhat resembling the "isoteniscope" has been introduced by A. W. C. Menzies[22] for measuring the lowering of vapour pressure by the addition of a solute. The "bulblet" is replaced by a graduated test-tube 30 cm. long and 2·3 cm. diameter, constricted to a neck through which vapour can be allowed to escape or solute to enter, and which can be closed by a small stopper at the end of glass rod. The capillary is inside the test-tube; it is sealed to an opening near the top of the tube, and passes down nearly to the bottom; it is graduated so that the difference in pressure inside and outside the tube can be measured from the height of the column of liquid driven up or drawn down in the capillary gauge-tube. The test-tube is heated by a vapour-jacket, arranged so that the vapour can be sent either into a reflux condenser at the side of the jacket, or (when this is closed) into the capillary gauge-tube, from which it escapes by bubbling through the liquid in the test-tube and out at the neck. This "blowing-through" process is continued until all dissolved gases have escaped, after which the stopper is inserted and the vapour diverted to the reflux condenser. If the liquid in the test-tube still contains dissolved gases, it gives a vapour pressure different from that of the solvent outside. But after two or three repetitions of the "blowing-through" process, occupying perhaps ten minutes, the difference of level shown in the gauge-tube is reduced to 0·1 mm. of liquid, corresponding with less than 0·01 mm. of mercury. Incidentally, this observation should settle finally the controversy as to the identity of the static and dynamic vapour pressures, since the difference between the static pressure of the liquid in the tube and the dynamic pressure of the liquid boiling in the jacket is shown to be too small to be measured.

The addition of small quantities of solute produces a very large difference of level in the gauge-tube, for example, the same quantity of solute that raises the boiling point by 0·1° produces a difference of level of 37, 55, and 37 mm. in water, alcohol, or benzene respectively. Molecular-weight determinations can therefore be carried out with greater ease and accuracy than by the ebullioscopic method, and with solutions so dilute that additional observations for the purpose of extrapolating to infinite dilution are quite unnecessary. A slight modification of the apparatus can be used for measuring the vapour densities of easily volatile liquids.[23]

Reference may be made here to the fact that O. F. Tower found

[22] *J. Amer. Chem. Soc.*, 1910, **32**, 1615; *A.*, ii, 94.
[23] A. W. C. Menzies, *ibid.*, 1624; *A.*, ii, 94.

in 1908[24] that static measurements of vapour pressure with the Morley gauge were not convenient for molecular-weight determinations, but that Krauskopf[25] obtained a few values for sugar and for sodium and potassium chlorides by saturating a current of gas with water-vapour from their aqueous solutions.

Osmotic Pressure of Aqueous Solutions of Sucrose.

A notable feature of the year's publication has been the appearance of a series of five papers on "The Relation of Osmotic Pressure to Temperature,"[26] in which H. N. Morse and his colleagues summarise the results of the work that they have carried out, during the past ten years, on the osmotic pressure of aqueous solutions of sucrose. As a result of repeated improvements of the experimental methods, the authors are now in a position to reject (1) all measurements in which any trace of leakage of sugar through the membrane could be detected, and (2) all measurements in which changes of concentration occurred during the measurements on account of (*a*) yielding of the manometer fittings under pressure, (*b*) dilution of the cell contents before closing or after opening the cell, or (*c*) filling the cell with solution not accurately adjusted to the temperature of measurement. As showing the permanence of the equilibrium and the perfection of the experimental methods, it may be mentioned that one cell, not specially selected, was kept for sixty days without showing any leakage of sugar or any measurable loss of rotatory power in the solution; moreover, the osmotic pressure, which at the beginning was 12·522 atm. (atmospheric pressure 1·013), was found at the end to be 12·522 (atmospheric pressure 1·016). Observations such as these render absurd the conventional criticism that semi-permeable membranes are ideal structures which can never be realised in practice.

The results obtained in 147 successful series of measurements are summarised in a group of tables, of which the most important is reproduced below:

Weight-normal concentration:

	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
Ratio of osmotic to gas pressure:										
t = 0°	(1 106)	1·061	1·061	1·060	1·0685	1·0765	1·083	1·093	1·104	1·115
5	1·082	1·063	1·058	1·059	1·067	1·074	1·084	1·093	1·102	1·115
10	1·082	1·060	1·059	1·060	1·066	1·073	1·083	1·092	1·102	1·113
15	1·082	1·061	1·061	1·059	1·068	1·073	1·083	1·093	1·102	1·115
20	1·084	1·062	1·060	1·060	1·067	1·073	1·084	1·093	1·103	1·115
25	1·084	1·059	1·060	1·059	1·065	1·071	1·083	1·093	1·102	1·113
Mean.	1·083	1·061	1·060	1·060	1·067	1·074	1·083	1·093	1·103	1·114

[24] *J. Amer. Chem. Soc.*, 1908, **30**, 1219; *A.*, 1908, ii, 811.

[25] *J. Physical Chem.*, 1910, **14**, 489; *A.*, 1910, ii, 688.

[26] *Amer. Chem. J.*, 1911, **45**, 91, 237, 383, 517, 554; *A.*, ii, 191, 375, 473, 701.

It will be seen that, with the exception of one solution of which the osmotic pressure was measured at a temperature within less than 0·2° of its freezing point, the values are absolutely steady from 0° to 25°. Over this range therefore Gay Lussac's law holds good absolutely, the osmotic pressure, like the pressure of a perfect gas, being directly proportional to the absolute temperature. The authors mention, however, that the ratios begin to fall off above 25°, and would probably drop to unity at a temperature below 100°. "Such conduct on the part of cane-sugar solutions can, of course, be ascribed with great plausibility to hydrates which are stable between 0° and 25°, but which gradually dissociate at higher temperatures."[27]

The experimental methods used in obtaining these results are described fully for the first time in four of the five papers now under review. The description can only be read with advantage in the original. It may be noted, however, that the authors were obliged finally to undertake the manufacture of their own porous pots by a novel process in which two clays, one with an excess and the other with a deficiency of binding material, were mixed, pressed into a cylinder, and turned up on a lathe; this was found to give much better cells than when attempts were made to mix clay with felspar in the usual manner.

A Laboratory Method of Measuring Osmotic Pressure.

A novel form of osmotic apparatus, so simple as to be readily available for a laboratory method of determining molecular weights, is described by E. Fouard.[28] In place of a porous pot, a collodion membrane is used,[29] deposited on a cylinder of metal gauze in order to avoid distension of the membrane. The membrane can be rendered semi-permeable by filling it with a solution of tannic acid and immersing in a solution of gelatin, or by depositing copper ferrocyanide in the membrane by a similar method. After providing the cell with a long, narrow, capillary tube, direct measurements of osmotic pressure can be made with solutions containing only about 1/1000 gram-molecule per litre; the density of such solutions is so nearly equal to that of water that no appreciable error is introduced when calculating the pressure from the hydrostatic pressure of the column of liquid in the capillary tube. As showing the efficiency of the membrane, it is stated that a solution of concentration 0·230 gave a head of 146·3 cm., which did not vary

[27] *Loc. cit.*, p. 603.

[28] *Compt. rend.*, 1911, **152**, 519; *J. de Physique*, 1911, [v], **1**, 627; *A.*, ii, 267.

[29] Compare J. H. Mathews, *J. physical Chem.*, 1910, **14**, 281; *A.*, 1910, ii, 487.

during twenty-five days, and that at the end of this time the concentration of the solution was 0·227.

In using the cells for practical osmometry, the most convenient method is to balance the osmotic pressure of the cell against that of an isotonic sugar solution. Values obtained in this way are shown in the following table:

Substance.	*c.* Concentration of solution.	*γ.* Concentration of sugar solution.	Molecular weight found, $M = 342c/\gamma$.	Molecular weight calculated.
Lactose	3·24	3·085	359·5	360·0
Dextrose monohydrate.	2·62	4·51	199·0	198·0
Mannitol	1·5	2·795	183·2	182·1
Asparagine	1·00	2·518	136·0	132·2
Quinine tartrate.....	0·25	0·1805	474·0	474·0
Quinol	1·00	3·02	112·6	110·0

These values appear to be more accurate than those usually obtained by the freezing-point or boiling-point method. It is stated that equilibrium is reached within about half an hour, the thinness of the film of collodion rendering the apparatus much more sensitive than when a porous pot is used.

Whilst the method thus appears to give excellent results with typical organic compounds, its application to salt-solutions has been adversely criticised by P. Girard and V. Henri,[30] on the ground that the momentary balancing of a salt-solution against a sugar-solution does not give a true comparison of their relative osmotic pressures, the results being vitiated from the very beginning by the permeability of the membrane to the salt.

Osmotic Pressure of Colloids.

A considerable number of measurements have been made recently of the osmotic pressure of colloids. W. M. Bayliss[31] has shown that solutions of Congo-red, a disodium salt of molecular weight 696, when separated from water by a parchment membrane, produce an osmotic pressure only slightly below that for single molecules of the calculated molecular weight; identical results have been obtained from measurements of vapour pressure; the temperature-coefficient of the osmotic pressure is also normal. These results cannot, however, be interpreted in the normal way, as the salt is very largely ionised, for example, to the extent of 80 per cent. at a concentration of 500 litres, and should therefore produce osmotic pressures from one and a-half to three times the calculated values.

[30] *Compt. rend.*, 1911, **153**, 946; *A.*, 1912, ii, 24.

[31] *Proc. Roy. Soc.*, 1909, B, **81**, 269; *A.*, 1909, ii, 648; *Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 23; *Proc. Roy. Soc.*, 1911, B, **84**, 229; *A.*, ii, 867.

The free acid of Congo-red can be prepared from the salt by dialysis as a blue colloidal solution. This exerts a small but definite osmotic pressure, corresponding with aggregates of 20 molecules in each colloidal particle. The blue solution is easily resolved by the ultra-microscope, giving a series of brilliant copper-coloured points, but these vanish when a drop of alkali is added, the Congo-red showing nothing but an occasional bright point. Very similar observations have been made by W. Biltz and his colleagues,[32] who found a molecular weight of 602 when measured against pure water, but 2333 when measured against a solution of the products of dialysis concentrated to equal electrical conductivity; the latter value, like the former, agrees approximately with that which would be given by single molecules of the normal size under these conditions.

The complex equilibria which result when salts such as Congo-red are submitted to dialysis have been investigated both theoretically and practically by F. G. Donnan.[33] He considers the conditions of equilibrium between a salt NaR with a non-penetrating anion and a salt such as NaCl, which can penetrate the membrane, and shows that the presence of a large quantity of NaR will almost entirely prevent the inward diffusion of the sodium chloride, although this can pass freely through the membrane in the opposite direction. If the non-dialysing electrolyte is separated by a membrane from pure water or from a weak alkali, sodium ions will diffuse out in the form of sodium hydroxide, and the solution inside the membrane will become acid; if the acid HR is weak, the membrane-hydrolysis may be very extensive. The diffusion of the ions has the effect of setting up differences of electrical potential on either side of the membrane. In the case of Congo-red, it is shown experimentally that the presence of this substance causes sodium chloride to distribute itself unequally on the two sides of the membrane, the concentration being higher on the side opposite to the Congo-red. Similar considerations apply in the case of sodium hydroxide. These inequalities of concentration and the electrical forces which they set up are sufficient to invalidate any attempts to deduce in the ordinary way the molecular weights of such substances from the osmotic pressures which they produce.

Conclusions somewhat similar to those of Donnan have been reached by B. Moore, H. E. Roaf, and A. Webster[34] in the course of a series of measurements of the osmotic pressure of casein in

[32] *Zeitsch. physikal. Chem.*, 1909, **68**, 357; 1910, **73**, 481; 1911, **77**, 91; *A.*, 1910, ii, 22, 693; 1911, ii, 702.

[33] F. G. Donnan, *Zeitsch. Elektrochem.*, 1911, **17**, 572; *A.*, ii, 848. F. G. Donnan and A. B. Harris, *Trans.*, 1911, **99**, 1554.

[34] *Bio-Chem. J.*, 1911, **6**, 110; *A.*, ii, 1072.

alkaline solutions. They show that the observed pressures cannot be due to saline impurities (ash) in the colloid, since the movement of the crystalloid associated with the colloid is against the osmotic pressure from the side of low pressure to that of high pressure; indeed, until the colloid is almost saturated by crystalloid, practically no alkali remains on the non-colloid side of the membrane. Alkali thus moves against osmotic pressure to the colloid side in order that it may there unite with the colloid. It is suggested that this union is the cause of the osmotic pressure, and that the purpose of the membrane is purely the mechanical one of holding together the colloidal aggregates, its apparent impermeability to the ions being quite fictitious; the authors consider that free ions pass through the membrane quite readily, whilst ions anchored to colloid are retained on the colloid side and exercise pressure. In the case of living cells, the varying concentrations of sodium, potassium, chlorine, and phosphate ions within and without the cell are regarded as an expression of specific affinities of the definite colloids of each particular cell type for these ions, and do not mean that there is a membrane acting as a closed gate to these ions.

J. Duclaux[35] finds a direct proportionality between the osmotic pressure and freezing-point depression of colloidal solutions of ferric and thorium hydroxides, but in the case of cellulose nitrate in acetone finds that there is no proportionality between osmotic pressure and concentration.

Properties of Solutions.

The completion of a series of nineteen "Studies of the Processes Operative in Solutions" affords an opportunity of referring, in continuation of preceding reports,[36] to the recent work of H. E. Armstrong and his co-workers on this subject. On the theoretical side,[37] the extreme complexity of the phenomena is emphasised. The view that water is a mixture of simple "water" or "steam" molecules with bulky, polymerised "ice" molecules (introduced by Röntgen and strongly supported by Tammann's skilful work in freezing out and isolating the two varieties[38]) is presented in a more elaborate form. The solvent is regarded as a complex mixture of molecules of many kinds, differing in complexity and in structure, and including isomeric molecules of various types. It is suggested that the equilibrium between them is so delicately balanced that it can be altered largely by very small changes in the conditions to

[35] *Compt. rend.*, 1909, **148**, 714; 1911, **152**, 1580; *A.*, 1909, ii, 377; 1911, ii, 588.

[36] *Ann. Report*, 1907, 17, 21; 1908, 21.

[37] H. E. Armstrong, *Chem. News*, 1911, **103**, 97.

[38] See *Ann. Report*, 1910, 2.

which the liquid is exposed. To such displacements of equilibrium, most of the changes taking place in solutions are attributed. In particular, the addition of a solute, whether an electrolyte or a non-electrolyte, is regarded as producing a breaking down of the more complex molecules and a large increase in the proportion of free hydrol.

On the experimental side, H. E. Armstrong and J. V. Eyre[39] have extended their earlier investigation of the precipitation of salts from their saturated aqueous solutions when these are mixed with non-electrolytes such as alcohol. These experiments have brought out the remarkable fact that the alcohols display a progressive increase in their precipitating effects as the molecular weight increases, and the chemical activity, as judged by the usual standards, diminishes. Propyl and ethyl alcohol are thus more effective precipitants than methyl alcohol, and *iso*butyl alcohol is still more efficient. The same order of efficiency is noticed when the alcohols are used to diminish the hydrolytic activity of an acid in sugar-inversion,[40] or to diminish the electrical conductivity of a salt.[41] The higher alcohols also possess a largely increased physiological activity, as is indicated by their ability to penetrate a barley-grain,[42] or to effect an entry into the tissue of a laurel leaf,[43] and there set up a great increase of enzymic activity.

Unlike the alcohols, salts have an accelerating effect in hydrolysis. F. P. Worley[44] and W. H. Glover[45] have obtained practically identical figures for the "apparent hydration values" of a series of salts, as deduced from their "concentrating effect" in the hydrolysis by acids of sucrose and of raffinose respectively. An increase of efficiency similar to that produced by the addition of a salt is observed when the relative concentration of the acid itself is increased. This increased efficiency, which takes place in spite of a decrease of molecular conductivity, has been studied in detail by H. E. Armstrong and E. Wheeler[46] in a comparison of the "Relative Efficiencies of Acids as Deduced from their Conductivities and Hydrolytic Activities."

W. H. Glover[47] has extended the work of Caldwell and Whymper[48] by examining the reciprocal effects produced by salts

[39] *Proc. Roy. Soc.*, 1910, A, **84**, 123; *A.*, 1910, ii, 832.
[40] H. E. Armstrong and F. P. Worley, *Chem. News*, 1911, **103**, 145.
[41] H. E. Armstrong and D. Crothers, *ibid.*, 121.
[42] A. J. Brown, *Ann. Report*, 1909, 11.
[43] H. E. Armstrong and E. F. Armstrong, *Proc.*, 1910, 334. See also *A.*, ii, 642, 918.
[44] *Trans.*, 1911, **99**, 349.
[45] *Ibid.*, 371.
[46] *Chem. News*, 1911, **103**, 33.
[47] *Trans.*, 1911, **99**, 379.
[48] *Proc. Roy. Soc.*, 1908, A, **81**, 117; *A.*, 1908, ii, 817.

on the rotatory power of a series of sugars and glucosides, and by these substances on the molecular conductivity of the salts. The effects produced by the sugars on the molecular conductivities of the salts were very strongly marked; the changes of rotatory power were smaller in magnitude, but with the exception of lactose and mellibiose were always in the same direction, from right to left, whatever the sign of the natural sugar or simple glucoside; the changes of rotatory power were smaller in the α-glucosides than in the more easily hydrolysed β-glucosides. Typical values for solutions containing 1 gram-molecule of sugar or glucoside and 1 gram-molecule of electrolyte dissolved in 50 gram-molecules of water are shown below:

Electrolyte.	Sugar or glucoside.	Molecular conductivity of electrolyte.	Reduction of molecular conductivity, per cent.	Values of $[\alpha]^{25}_{Hg.}$	Alteration in degrees.	Alteration, per cent.
Sodium chloride	Dextrose	59·44	29·5	+62·82°	−0·35	−0·56
	α-Methylglucoside	56·50	33·0	+185·98	−0·52	−0·27
	β-Methylglucoside	56·80	32·6	−40·55	−0·74	−1·86
	Sucrose	44·16	47·6	+76·94	−1·14	−1·46
Sodium nitrate	Dextrose	53·28	29·0	+62·78	−0·39	−0·62
	α-Methylglucoside	50·94	32·1	+186·39	−0·11	−0·06
	Sucrose	39·68	47·1	+77·52	−0·56	−0·72

Anomalous Curves of Molecular Conductivity.

The appearance in a curve of molecular conductivity of a maximum in the higher ranges of concentration, with an intermediate minimum separating it from the usual maximum at infinite dilution, was first noticed in the case of solutions of salts in amines and in liquid ammonia.[49] It has since been observed in aqueous solutions[50] and in liquid sulphur dioxide,[51] and appears, therefore, to be a fairly general phenomenon when suitable conditions can be attained. In the case of solutions of potassium iodide, potassium bromide, ammonium thiocyanate, and tetramethylammonium iodide in liquid sulphur dioxide, the maximum and minimum become more and more pronounced as the temperature of experiment is raised from −33·5° to +10°. This is in accordance with the view of Franklin and Gibbs[52] that the maximum in concentrated solutions is due to the "autolytic conductivity" of the liquefied salt, since this would become relatively more important as the affinity between salt and solvent became weakened with rising temperature.

[49] *Ann. Report*, 1909, 29. [50] *Ibid.*, 1910, 24.
[51] E. C. Franklin, *J. Physical Chem.*, 1911, **15**, 675; *A.*, ii, 1052.
[52] *Ann. Report*, 1909, 30.

Absorption Spectra of Inorganic Salts.

With the exception of a few measurements in the visible region, made with the help of a spectrophotometer,[53] or a tintometer,[54] nearly all the recent work on absorption spectra[55] has been carried out with the help of the photographic method of Hartley and Huntington. The absorption curves plotted from the photographs have been of great value in studying the origin of colour, and in investigating the constitution of labile compounds. From the quantitative point of view they have certain very marked disadvantages. The most conspicuous of these is the wide variation which exists between the intensity of the lines in different regions of the arc spectra which are employed as sources of light. Even if a uniform spectrum were available, the form of the absorption curve would be influenced largely by the varying sensitiveness of the photographic plate to light of different wave-lengths. Since there is no proportionality between the density of the image and the time of exposure, the latter becomes a factor of great importance in determining the form of the curve; thus, it is well known that under-exposure increases enormously the contrast between the strong and weak parts of the spectrum, thereby exaggerating the maxima and minima in the absorption curves, and in extreme cases producing in weak parts of the spectra the apparition of absorption bands, which disappear when the exposure is increased.

The recognition and elimination of these sources of error are the most valuable feature of a series of four papers on "The Absorption of Light by Inorganic Salts," by R. A. Houstoun and his colleagues.[56] Measurements were made, in the case of aqueous solutions of a series of salts of cobalt and nickel, of the molecular extinction-coefficients in the infra-red, in the visible, and in the ultra-violet regions, as given by the formula:

$$I = I_0\, 10^{-Acd},$$

where the original intensity of the light is I_0, the final intensity is I, c is the concentration of the solution in gram-molecules per litre, d the length of path traversed in cm., and A the molecular extinction-coefficient. A is, of course, a function of λ, the wave-length of the light in question, and may also vary with the concentration c of the solution.

The measurements in the infra-red were made with the help of

[53] See, for instance, A. Hantzsch and W. H. Glover, *Ber.*, 1906, **39**, 4153; *A.*, 1907, i, 101.

[54] N. V. Sidgwick and H. T. Tizard, *Trans.*, 1908, **93**, 187.

[55] *Ann. Report*, 1910, 79; 1909, 63; 1908, 9; 1907, 5; 1906, 26; 1905, 9.

[56] *Proc. Roy. Soc. Edin.*, 1911, **31**, 521, 530, 538, 547; *A.*, ii, 785, 786.

a Rubens linear thermopile provided with twenty iron-constantan junctions on a length of 2 cm., and a Du Bois-Rubens ironclad-galvanometer; the spectroscope was fitted with glass lenses and prisms, and was calibrated by using the absorption-maxima of water in the infra-red at 0·966μ, 1·500μ, 1·956μ, and the minimum at 1·708μ; the source of light was a Nernst filament carrying a current of 1 ampere, stray heat being eliminated by using two spectroscopes in series with one another.

For work in the visible region a spectrophotometer of the Hüfner type[57] was used, light from the same portion of an incandescent mantle being passed through water and through the solution, and viewed in the form of two adjacent spectra, the brighter spectrum being reduced to equality in the usual way by rotating a Nicol prism.

The most novel feature of the work was the arrangement for measuring the absorption-coefficients in the ultra-violet region. The essential principle in developing a photographic method of measurement was that two beams of light falling on adjacent parts of the same photographic plate should produce equal blackening in equal time; this prohibited the use of a rotating sector for diminishing the light, since equal density produced in half the time would not in the case of a photographic plate imply a two-fold intensity. The method adopted was to throw on the slit of an ordinary spectrograph two beams of light, one originating in a plate of ground quartz brightly illuminated by an iron arc and passing through the solution before reaching the slit, whilst the other, passing directly to the slit, originated in a similar quartz plate, the illumination of which was diminished by placing it at an increased distance from the arc. Photographs were taken with the quartz plates in a series of standard positions, and for each position the wave-lengths were noticed at which the direct light had been diminished to equality with that passing through the solution; in some cases as many as five such points were given on one exposure, indicating at least two minima and two maxima in the curve for A as a function of λ.

On plotting out such curves the cobalt salts showed a steadily increasing absorption-coefficient in the infra-red up to 1·3μ, a strong maximum at 0·5μ in the visible region, and a progressive increase of absorption in the furthest ultra-violet region. In the case of the nickel salts a maximum absorption was actually reached in the furthest measurements in the infra-red region at 1·2λ; a second and a third maximum were found at 0·7μ and 0·4μ, in the extreme red and violet regions of the visible spectrum respectively. Addi-

[57] *Phil. Mag.*, 1908, [vi], **15**, 282.

tional bands due to the negative radicle were observed in the case of the iodides, bromides, and nitrates.

The absorption spectra of cobalt salts in the visible and ultra-violet regions were also included by H. C. Jones and his colleagues in their recent work on the absorption spectra of salts.[58] The ultra-violet absorption, which is exceedingly slight in the case of the sulphate, is attributed to molecular complexes. The band in the green, which persists in all cobalt salts in all solvents, is regarded as a specific property of the cobalt atom or radicle; in aqueous solutions the width of the band increases with increasing concentration, with rising temperature, and with the addition of hygroscopic salts such as calcium chloride; in each case the effect is attributed to the greater freedom of the atom, resulting from the breaking down of hydrates. The absorption of red light is very slight in the case of aqueous solutions, unless the concentration is large, the temperature high, or the solution mixed with relatively large quantities of dehydrating salts; but solutions in which these conditions are fulfilled show absorption bands which are attributed to simple compounds of solvent and solute. These bands vary very much with the solvent, and are altogether absent when glycerol is used; addition of 5 to 10 per cent. of water to solutions of cobalt chloride in methyl alcohol, ethyl alcohol, or acetone causes the bands characteristic of these solvents to break up and give place to the bands characteristic of concentrated aqueous solutions, but further dilution causes the bands to disappear altogether, since dilute aqueous solutions do not show any marked absorption in this region.

In the majority of cases, in marked contrast with the important effects produced by changes of solvent, the nature of the colourless negative radicle has but little influence on the absorption spectra of coloured salts. An exception is found in the case of the uranium salts, the properties of which are described in the last paper of the series. It is there shown that uranyl nitrate gives an absorption-spectrum differing widely from that of the other uranyl salts; on adding sulphuric acid to solutions of the nitrate, the spectrum is converted into that of the sulphate by the *gradual* shifting of the bands; similar *gradual* changes take place when other acids are added. Equally marked differences are observed in the spectra of uranous salts in water, the alcohols, acetone, and glycerol, but it is remarkable that here again, when mixed solvents are used, *both* sets of bands appear, in striking contrast to the gradual shifting observed when salts with different acid radicles are mixed.

[58] *Amer. Chem. J.*, 1907, **37**, 126, 207, 244; 1909, **41**, 163, 276; 1911, **45**, 1, 113; *A.*, 1907, ii, 147, 211; 1909, ii, 359; 1911, ii, 166.

In the case of neodymium chloride the effects produced by varying the solvent are specially remarkable, the "water"-band at λ 4274 being resolved in other solvents into two, three, or a larger number of separate bands. In this case the gradual change from the "water" to the "glycerol" bands constitutes an exception to the general rule, according to which both sets of bands appear together in mixed solvents; the gradual change observed on adding nitric acid to solutions of neodymium acetate is, however, in agreement with the observations on the uranyl salts described above.

Salts of nickel, copper, iron, chromium, praseodymium, and erbium are also included in the scope of this investigation.

The ultra-violet absorption spectra of aqueous solutions of a specially pure specimen of neodymium chloride have been investigated independently by G. P. Baxter and T. S. Woodward.[59]

Photochemistry.

From the large number of papers dealing with the influence of light on chemical change which are dealt with in the Abstracts for the year, those of L. Bruner may be selected for special mention. This author has already studied the effect of light on the change of maleic into fumaric acid,[60] and has shown that whilst the action of bromine on maleic acid in the dark consists exclusively in a slow addition governed by the bimolecular law, the same agent in presence of light brings about isomeric change in the acid, fumaric acid being precipitated almost immediately when the mixture is exposed to sunlight. The change, which is brought about by the blue rays, is not influenced to any marked extent by small changes of temperature; although assisted by mineral acids, it is checked by the presence of fumaric acid, but is practically quantitative if carried out in bright sunlight with a relatively large proportion of bromine, for example, 1 molecule of bromine to 500 molecules of maleic acid. As the addition of uranium salts or dichromates does not set up isomeric change even in sunlight, the action is evidently dependent on the chemical rather than the physical properties of the bromine, whilst its selective character is further shown by the fact that it is not initiated by iodine, chlorine, iodine mono- or tri-chloride. It can be explained by addition of bromine, elimination of hydrogen bromide, and photochemical reduction of the resulting mixture of bromofumaric acid with hydrogen bromide.

The later papers[61] deal with the photobromination of toluene. In

[59] *J. Amer. Chem. Soc.*, 1911, **33**, 270; *A.*, ii, 351.

[60] L. Bruner and M. Królikowski, *Bull. Acad. Sci. Cracow*, 1910, 192; *A.*, i, 9.

[61] L. Bruner and S. Czarnecki, *ibid.*, 516; *A.*, ii, 241. L. Bruner and Z. Lahociński, *ibid.*, 560; *A.*, ii, 242.

this case much difficulty was experienced in securing conditions such that the bromination should cease as soon as the light was removed. The chemical catalyst, which usually carried on the action for some hours, is an oxygen compound. It can be destroyed by keeping the partly brominated toluene at 100° during two hours, or at atmospheric temperatures during fifteen to eighteen hours, or by the addition of oxidisable substances, such as iodine or hydrogen bromide. On the other hand, the side-chain bromination of toluene can be enormously accelerated by the action of ozonised oxygen, the action then proceeding with great rapidity, even with concentrated solutions and in darkness. The catalyst is therefore, in all probability, an oxidised derivative of bromine. In making experiments on the influence of light, it is most convenient to steady the action by means of a trace of iodine (about 1 milligram per litre). Unlike ordinary chemical changes, the photochemical action is independent of the concentration of the bromine, of which equal quantities are used in equal times throughout the whole course of the action; the velocity is, however, proportional to the concentration of the toluene, when this is varied by the addition of a solvent, and varies considerably according to the nature of the solvent. The velocity is also influenced by the temperature, although the rate of increase is only half as great as in the case of the slow action which takes place in darkness. Unlike the isomeric change of malic into fumaric acid, the bromination of toluene appears to be facilitated by all the different rays emitted by the mercury arc.

Dynamic Allotropy.

Allotropy, like polymorphism, has usually been regarded as being of one of two alternative types. In some cases the allotropy is *enantiotropic*, the different varieties of the element being convertible into one another by changes of temperature, as in the case of grey and white tin (transition temperature 18°) or α-, β-, and γ-iron (transition temperatures 766° and 895°). In other cases the allotropy is *monotropic*, one variety being metastable at all temperatures, and tending constantly to pass into some more stable form; such a case is that of explosive antimony.

In recent years a third type of allotropy has been recognised, to which the name *dynamic allotropy* has been given. In cases of this kind the different allotropes can exist in equilibrium with one another in definite proportions over a range of temperatures, and not at the transition-temperature only. The phenomena are, in fact, similar to those of dynamic isomerism in every respect, except that they are observed in elements instead of in compounds.

The first case of dynamic allotropy to be clearly recognised was

that of liquid sulphur, which has been shown by the work of A. Smith and his colleagues in a series of papers[62] to be a mixture of light, mobile, soluble S_λ, with dark, viscous, insoluble S_μ, in definite, measurable proportions, for example, 3·7 per cent. of S_μ at 114·5°, the "natural freezing point" of the mixture. This freezing point varies with the nature of the solid separating and with the proportion of S_μ in the liquid. The "ideal freezing points," when no S_μ is present, and the "natural freezing points," when an equilibrium-proportion of the insoluble S_μ is present in the liquid, are now given for three varieties of the element by A. Smith and C. M. Carson[63] as follows:

	Ideal F. p.	Natural F. p.
Rhombic sulphur, S_1	119·25°	114·5° (3·6% S_μ)
Prismatic sulphur, S_2	112·8	110·2 (3·4% S_μ)
Nacreous sulphur,[64] S_3 ...	106·8	103·4 (3·1% S_μ)

The heat content of the various forms of sulphur has been determined by G. N. Lewis and M. Randall,[65] who give for the heats of fusion:

	To S_λ.	To $S_\lambda \rightleftarrows S_\mu$.
Rhombic	14·5	14·9
Monosymmetric	11·1	11·5

and for the heat of transformation in the liquid state from S_λ to S_μ, 13 cals.

The phenomena of dynamic allotropy have also been recognised in the case of phosphorus by A. Smits and H. L. de Leeuw.[66] The phosphorus was purified by distillation in a vacuum, and then by fractional crystallisation of the melted substance in the exhausted receiver; it was then perfectly colourless and coarsely crystalline, and melted at 44·0° with a range of less than 0·02°. This is regarded as the unary melting point of white phosphorus, as it exists in stable equilibrium with the liquid. After keeping the solid for a day at 40°, it melted at 43·92—43·96°, over a range of 0·04°; after keeping the liquid for some time at 46°, freezing took place at 43·89—43·84°, and had a range of 0·05°. These observations show that no marked disturbance of the equilibrium takes place in the liquid or solid in the immediate neighbourhood of the freezing point.

[62] *A.*, 1903, ii, 139, 284; 1905, ii, 382, 580; 1906, ii, 157; 1907, ii, 20, 451; *Ann. Report*, 1907, 61; 1908, 39. Compare H. R. Kruyt, *Zeitsch. physikal. Chem.*, 1908, **64**, 513; *A.*, 1908, ii, 1038.

[63] *Zeitsch. physikal. Chem.*, 1911, **77**, 661; *A.*, ii, 977.

[64] Nacreous sulphur, discovered by Gernez, may be prepared in lustrous, needle-shaped crystals by heating sulphur to 150°, cooling to 98°, and making it crystallise by scratching the containing tube with a glass rod.

[65] *J. Amer. Chem. Soc.*, 1911, **33**, 476; *A.*, ii, 371.

[66] *Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 822; *A.*, ii, 263.

When, however, the phosphorus was heated for some time at 100° and suddenly quenched to 44° by immersion in cold water, it behaved in a very different way; the fusion was already overcooled at 44°, since when crystallisation was started by grafting at 43·5° its temperature rose at once to 45·05°; crystallisation then took place over a range of 1·8°, from 45·05° to an estimated temperature of 43·25°. In another experiment crystallisation began at 46°, and took place over a still wider range of temperature. By heating to 100° the behaviour of the phosphorus had therefore been changed from that of a homogeneous liquid crystallising at a constant temperature to that of a mixture of allotropes crystallising over a range of temperatures. This condition does not persist for any length of time, as the solid was found to re-melt over a range of only 0·13°, from 43·97—44·10°, indicating that a normal condition had almost been reached during the short time occupied by the two experiments.

Mercury was found to give no indication of dynamic allotropy, its melting point being both sharp and constant, whether quenched from +300° or warmed up from −80°. Highly purified tin was found to behave in the same way as phosphorus, solidifying under some conditions as a pure substance, but behaving as a complex mixture when crystallised by sudden quenching.

The allotropy of phosphorus is much more complex than that of sulphur,[67] and it is scarcely possible at the present time to state conclusively under what conditions the different solid varieties of the element are stable. P. Jolibois[68] finds that red phosphorus (D 2·18) is converted into dense violet or metallic phosphorus (D 2·37) at temperatures from 250° upwards if iodine is added as a catalyst, but that above 450° red phosphorus is the stable form, until at 610° it melts to liquid white phosphorus. E. Cohen and J. Olie, jun.,[69] on the other hand, consider that red phosphorus is an isomorphous mixture or solid solution of the white and metallic forms. Smits and de Leeuw[66] elaborate this view by representing white, red, and metallic phosphorus as three series of solid solutions in a complex equilibrium-diagram. A parallel case of isomorphism amongst dynamic isomerides has been studied by E. G. Laws and N. V. Sidgwick.[70]

T. M. Lowry.

[67] See, for instance, Hittorf, *Pogg. Ann.*, 1865, **126**, 193; Lemoine, *Ann. Chim. Phys.*, 1871, [iv], **24**, 129; Troost and Hautefeuille, *Ann. Chim. Phys.*, 1874, [v], **2**, 145; *A.*, 1874, 769; D. L. Chapman, *Trans.*, 1899, **75**, 734.

[68] *Compt. rend.*, 1909, **149**, 287; 1910, **151**, 382; *A.*, 1909, ii, 726; 1910, ii, 846.

[69] *Zeitsch. physikal. Chem.*, 1910, **71**, 1; *A.*, 1909, ii, 998.

[70] *Trans.*, 1911, **99**, 2085.

INORGANIC CHEMISTRY.

In the Annual Report of the work of 1911, some variation has been made in the subjects in which a summary has been attempted. This variation is due to the special attention which has been given to particular branches of inorganic chemistry during the course of the year. Other subjects might have been selected, but in some of them much more experimental work is necessary before a useful survey could be made. One such subject, for instance, the theory of the lead chamber process, has been investigated for some years past by Raschig; his results have been criticised by Divers, but at the present time the subject is in so chaotic a state that only further experiment can decide which, if any, of the substances stated to be the intermediate products are really effective in the transformation.

No summary of the year's work can be complete without special reference to the very important theory put forward by Professor T. W. Richards[1] on the compressibility of atoms. The experimental evidence adduced in favour of the theory is of the strongest kind, and there is little doubt that other workers will co-operate in accumulating still further proofs of the theory.

Atomic Weights.

The chief alterations recommended by the International Committee on Atomic Weights[2] up to October, are that on the strength of two papers by Richards and Hönigschmid the atomic weight of calcium is decreased from 40·09 to 40·07. The atomic weight of iron likewise is decreased from 55·85 to 55·84. Mercury has been increased from 200·0 to 200·6 on the work of Easley, a change which one may hope is not premature. Since the report of the Committee has been published, an interesting redetermination of the $KClO_3$:KCl ratio has appeared.[3] The determination of the products of decomposition of potassium chlorate is a matter of great difficulty if the decomposition is effected by heating.

[1] Faraday Lecture, *Trans.*, 1911, **99**, 1201. [2] *Ibid.*, 1867.
[3] A. Stähler and F. Meyer, *Zeitsch. anorg. Chem.*, 1911, **71**, 378; *A.*, ii, 881.

This salt occludes water to a considerable extent when crystallising, and this water cannot be removed below the temperature at which the salt itself is slightly decomposed. The authors of the paper surmount the difficulty by weighing the chlorate and then fusing it in an apparatus of quartz, the water given off being collected and weighed. By subtracting the weight of this water from the weight of original chlorate taken, the weight of the dry salt is obtained. The chlorate was decomposed by hydrochloric acid at 0°; the chlorine and oxides of chlorine were, as a precaution, collected in a vessel containing liquid air, and the residual chloride was dried and weighed. The liquefied gases which were condensed were allowed to evaporate, and the slight residue of potassium salt which had passed over in spray was converted into perchlorate and weighed. The ratio, assuming $K:Cl=1\cdot102641$, gives $K=39\cdot097$ and $Cl=35\cdot458$, atomic weights which differ only in the third place of decimals from the accepted values.

The work of Flint [4] on the supposed fractionation of tellurium, in which an atomic weight of 124·32 was obtained, has been repeated [5] on material lent for the purpose by Marckwald. The conditions of Flint's experiments were reproduced as far as possible, and after four successive precipitations of the tetrachloride by water, the atomic weight, determined by conversion of the element into the bromide, showed no alteration. This treatment in the hands of Flint gave a drop of a whole unit in the atomic weight. In further similar treatment of the material, the oxide was observed to have a yellow colour, which Flint also mentions as occurring in his fractionation. The authors showed that this colour was due to the presence of trioxide, the formation of which was traced to the use of hydrochloric acid which had been exposed to light and hence contained chlorine. By employing tellurium trioxide instead of the dioxide in Flint's atomic-weight determination, an apparent atomic weight of 118·32 was obtained. If, therefore, Flint's dioxide contained trioxide, the lowering of his atomic weights is explained.

Electric Discharge and Chemical Action.

The work of Sir J. Dewar and H. O. Jones [6] on carbon monosulphide, which, in a polymerised state, was shown to be formed by the action of nickel carbonyl on thiocarbonyl chloride, has been continued with very interesting results. The new method [7] employed was the action of the silent discharge on the vapour of carbon

[4] *Amer. J. Sci.*, 1910, [iv], **30**, 209; *A.*, 1910, ii, 845.
[5] A. G. Vernon Harcourt and H. B. Baker, *Trans.*, 1911, **99**, 1311.
[6] *Proc. Roy. Soc.*, 1910, A, **83**, 408, 526; *A.*, ii, 408.
[7] *Ibid.*, 1911, A, **85**, 574; *A.*, 1912, ii, 46.

disulphide. This substance was purified carefully by four distinct methods, the same result being obtained whichever method was used. The substance collected in a U-tube, cooled by liquid air, was at first white, but soon became brown, the transformation being accompanied by a flash and sometimes by a detonation sufficiently violent to shatter the tube. If the condenser was cooled to $-210°$, the deposit was quite white, but even at this low temperature transformation took place in fifteen minutes. No electric disturbance was found to accompany the transformation. The gaseous substance produced in the silent discharge tube was found to be still gaseous at $-120°$. It disappeared when passed over cocoa-nut charcoal. The brown substance was analysed, and it was found to correspond almost exactly with the formula $(CS)_n$, thus disproving the assertion of Losanitsch [8] that the brown substance which he prepared in a similar way was a polymeride of carbon disulphide. The most remarkable of the chemical reactions of the monosulphide is its action on concentrated sulphuric acid. This becomes yellow, then orange-red, and then deposits sulphur, a brisk effervescence of gas, consisting of carbon monoxide, carbon dioxide, and sulphur dioxide, taking place all the time. The properties of the monosulphide correspond closely with those of the brown substance obtained by Sidot [9] by the action of light on carbon disulphide.

The research which has perhaps aroused more interest and caused more discussion than any other published during the year, is one on the chemically active modification of nitrogen.[10] It is well known that after an electric discharge has been passed through a vacuum tube containing small quantities of gas, an after-glow is seen, which may last for some minutes. It has often been suspected that the residual glow might be due to a recombination of atoms to re-form the molecules which had been broken up by the discharge. Strutt brings evidence to show that in the case of nitrogen the gas has properties which are not possessed by ordinary nitrogen. A current of nitrogen at low pressures was drawn through a bulb through which a high-tension discharge was being passed. The glowing gas was subjected to various treatment in a tube some 20 cm. further on. The glow was found to be destroyed when the tube was heated, but re-appeared when the gas reached a cooler part of the tube. Ordinary phosphorus was converted into amorphous phosphorus, an increase in weight of 15 mg. being found after the passage of two and a-half litres of the nitrogen. Iodine gives

[8] *Ber.*, 1907, **40**, 4656; *A.*, 1908, ii, 32.

[9] *Compt. rend.*, 1872, **74**, 179; *A.*, 1875, 1236.

[10] R. J. Strutt, *Proc. Roy. Soc.*, 1911, A, **85**, 219 (Bakerian Lecture); *A.*, ii, 482; *ibid.*, 1911, A, **86**, 56.

a bright blue glow, sulphur and arsenic give faint blue and green glows, selenium, antimony, and carbon are without action. Sodium and mercury give the nitrides, line spectra of the metals being developed, and line spectra of cadmium, zinc, lead, magnesium, and potassium are also obtained when the glowing nitrogen is passed over the metals. Hydrogen merely acts as a diluent of the glow, no ammonia being observed; oxygen destroys it, apparently without any oxidation taking place. On mixing the glowing nitrogen with nitric oxide, nitrogen trioxide is produced, which can be condensed as a blue solid in liquid air. By weighing the nitrogen trioxide formed, an estimate of the percentage of nitrogen rendered active was arrived at; it was 2·46. A similar estimate obtained from the absorption by phosphorus gave a percentage of 0·48.

It is extremely difficult to estimate the value of the discovery, for a discovery it undoubtedly is, and an important one. Whether it is really a chemical action, as the author believes, resulting in the splitting up of nitrogen into charged atoms, true chemical ions, much further work will be necessary in order to decide. The duration of the active character after the electrical discharge is stopped is very small. The visibility of the glow, and presumably its active character, is not affected on passing through an electric field of 3000 volts per centimetre, and hence gaseous ions cannot be responsible for its behaviour. It must be remembered that all the chemical actions described can be brought about by the electric discharge, and it is conceivable that some hitherto unknown electrical influence might survive the passage through an electric field. The author is probably right in assuming that the fact that no liquefaction takes place at the temperature of liquid air proves that no polymeride of nitrogen has been formed. If liquid hydrogen were used as a condensing agent, something different from ordinary liquid nitrogen might be obtained. It is possible that some support may be gained for the author's atomic nitrogen hypothesis by the behaviour of the glowing gas on cooling. The brightening of the glow as the gas was cooled may be due to the increased number of atoms undergoing recombination, or, on the other hand, it may only be caused by the increased number of glowing particles in unit volume. The effect of heat in destroying the glow would be difficult to understand on the atomic nitrogen theory, whilst it recalls very vividly the behaviour of a vacuum tube through which a discharge is actually passing. If a point of the tube is heated, the luminosity of the discharge is visible only on either side of the heated surface. This phenomenon has been noticed by the writer with tubes containing oxygen, nitrogen, bromine, iodine, and

helium. Whatever their ultimate explanation, there is no doubt of the very great interest attaching to the experiments.

Catalytic Action.

Since the time when Berzelius first introduced the term catalysis into chemical literature, the efforts of chemists have continued, without ceasing, to endeavour to explain the large number of chemical actions which, because they are not understood, are called catalytic. One such class of actions which seems as far off as ever as regards an explanation, is the influence of finely divided metals. The action of iron and nickel on the behaviour of hydrogen with various substances has been studied by Neogi and Adhicāry.[11] The authors were unable to confirm the statement of Ramsay and Young,[12] that iron was able to bring about some union between nitrogen and hydrogen, although reduced iron as well as iron wire were tried, and at varying temperatures and different degrees of dryness. Nickel in various forms was found to be equally ineffective. Reduced nickel was, however, able to induce the reduction of nitric oxide by hydrogen, ammonia being produced in almost quantitative amount. The reaction began at 300°, but once started, it would go on at as low a temperature as 120°. Hydrogen sulphide and hydrogen phosphide were also produced by the interaction of hydrogen and reduced nickel with the oxides of the elements. It is probable that in the last two cases nickel sulphide and nickel phosphide were produced as intermediate compounds.

In order to test the truth of a theory of Sir J. J. Thomson [13] that the catalytic effect of water vapour was due to its high specific inductive capacity, Klein [14] has confirmed and extended some previous experiments on the influence of various liquids on the dry hydrogen sulphide and sulphur dioxide mixture.[15] Eight carefully dried organic liquids were found to bring about an immediate deposition of sulphur, eight produced a gradual change, while ten more were without effect. The author can find no relation between the specific inductive capacity of the liquids and their activity as catalysts, and he believes that his experiments support in all cases an intermediate compound theory of catalysis.

The decomposition of hydrogen peroxide by the agency of chromic acid has been the subject of discussion between Spitalsky [16] and

[11] *Zeitsch. anorg. Chem.*, 1910, **69**, 209 ; *A.*, ii, 107.
[12] *Trans.*, 1884, **45**, 93.
[13] *Phil. Mag.*, 1894, [v], **36**, 321.
[14] *J. Physical Chem.*, 1910, **15**, 1 ; *A.*, ii, 200.
[15] H. B. Baker (Wilde Lecture), *Mem. Manchester Phil. Soc.*, 1909, **53**, 3.
[16] *Ber.*, 1910, **43**, 3187 ; *A.*, ii, 37.

Riesenfeld.[17] The former regarded it as purely a catalytic action brought about by the mixture of chromium tri- and sesqui-oxides. The latter, however, shows that the action is a normal one, proceeding according to the equation:

$$4H_2Cr_2O_7 + 7H_2O_2 = Cr_2(Cr_2O_7)_3 + 11H_2O + 5O_2.$$

A research of a very interesting character by D. L. Chapman and H. E. Jones[18] deals with the decomposition of ozone. It was stated many years ago by Shenstone[19] that very dry ozone is much less stable than the moist gas. Armstrong suggested that the cause of the rapid decomposition of the dried ozone was that traces of oxides of nitrogen were formed from small quantities of nitrogen in the oxygen used. The authors have proved that this supposition is correct. In the dried state the oxides of nitrogen act as catalysts in decomposing the ozone, whilst in presence of moisture these oxides are removed from the sphere of action by being converted into nitric acid, which is deposited on the walls of the vessel. It was shown that ozone can be kept for some weeks without much decomposition even in presence of phosphoric oxide, but if the sealed tubes containing the phosphoric oxide were heated to 100° the catalytic effect of the drying agent was very considerable. In the actual experiments, therefore, the end of the tube containing the oxide was made to project from the steam jacket, so that it remained cool while the rest of the tube was kept at 100°. It would doubtless have been better if this part of the tube had been sealed off before the experiment was commenced, but in order to do this a constriction would have been necessary, which would have very much increased the length of time necessary for drying the gas. The results of six experiments are given, in which tubes containing moist ozone were heated under the same conditions as tubes containing the gas which had been kept for periods of from ten days to three weeks in contact with the drying agent. No appreciable difference in the amount of decomposition could be found, and it must be concluded that this action must be added to the list of those in which the presence of moisture is not necessary. The other chemical actions in this category, as far as the writer is aware, are (1) the combustion of cyanogen,[20] (2) the combustion of carbon disulphide,[21] (3) the combustion of marsh gas and ethylene,[22] (4) the action of the halogens on mercury.[23] The authors give a new method for the preparation of very pure phosphoric oxide, which

[17] *Ber.*, 1911, **44**, 137; *A.*, ii, 107.
[18] *Trans.*, 1911, **99**, 1811.
[19] *Ibid.*, 1897, **71**, 471.
[20] H. B. Dixon, *ibid.*, 1886, **49**, 384.
[21] H. B. Baker, *ibid.*, 1894, **65**, 616.
[22] Bone and Wheeler, *ibid.*, 1906, **89**, 852.
[23] W. A. Shenstone, *ibid.*, 1897, **71**, 471.

for its simplicity and effectiveness will be much appreciated by those who have hitherto spent many hours in obtaining 1 or 2 grams of the distilled oxide from 100 grams of the commercial substance.

The Rusting of Iron.

Still more evidence has been brought to bear on this problem during the past year, but it cannot yet be said that agreement as to the mechanism of the action has been reached. There is no doubt that pure iron does not rust in contact with pure oxygen and pure water,[24] and further that as much as one-fifth of the oxygen can be replaced by carbon dioxide without rusting taking place.[25] Commercial iron, however, behaves quite differently, and it is with regard to the rusting of this iron, containing perhaps as little as 0·3 per cent. of impurity, that so much discussion has taken place. The recent paper of Dunstan and Hill[26] throws much new light on the subject. The authors have sought for an explanation of the fact that the presence of many substances in solution prevents rusting, and they have established an important relation between the inhibiting effect of such substances and the power of such substances to render iron passive to diluted nitric acid and to copper sulphate solution. It was shown that the passive state of iron could be produced by allowing the metal to remain for comparatively long periods in solutions of highly oxygenated salts, such as chromic acid, and the permanganate, chlorate, bromate, iodate, and arsenate of potassium, as well as hydrogen peroxide and nitric acid. Besides these, the hydroxides of sodium, potassium, ammonium, and barium, and the carbonates of sodium and potassium were found to induce the passive condition of the metal. The iron was passive to nitric acid (D 1·2) and to copper sulphate, but it should be noticed that the passivity induced by some of these solutions was of comparatively short duration. In all cases, however, it was found that those solutions which prevented rusting also produced the passive state, and since it was also proved that dilute acids, even carbonic acid, destroy the passivity, many previous results, such as those of Friend[27] and of Moody,[28] can be explained without the supposition that carbon dioxide is the primary cause of rusting. It must be pointed out, however, that although these two workers used iron which had been made passive by potassium hydroxide and chromic acid respectively, it does not follow that the iron in their experiments would have rusted if it had not been so treated; indeed, Dunstan and Hill describe an experiment in

[24] Lambert and Thomson, *Trans.*, 1910, **97**, 2426.
[25] Lambert (*priv. comm.*).
[26] *Trans.*, 1910, **99**, 1835.
[27] *Proc.*, 1910, **26**, 179.
[28] *Trans.*, 1906, **89**, 720.

which commercial iron immersed in water in contact with oxygen remained bright for six months, and it was only at the end of this period that rusting began. It might quite reasonably be suggested that the cause of rusting in this experiment was not the slow diffusion of dissolved oxygen, which according to the authors required six months to traverse a 14-inch tube, but that it was really due to carbon dioxide produced by the oxidation of the india-rubber stoppers or the paraffin which covered them. The authors propose no theory of rusting, but they argue strongly against the so-called electrolytic theory of Walker, Cederholm, and Bent. This might be called a solution-tension theory, but there is in it no element of true electrolytic action. Dunstan and Hill's experiments support the really electrolytic theory of Tilden.[29] The clearest and most forcible statement of this theory has been given by Armstrong.[30] For rusting to take place, iron must not be uniformly pure; one part must be capable of becoming electronegative to the other, and also the water must be sufficiently impure to be a conductor. If the iron is pure or the water is pure, no rusting can take place. Hence, pure iron in water containing carbon dioxide would not rust, neither would iron containing iron carbide in ideally pure water, because in neither case could an electric current be started. Armstrong does not deal, however, with the question of the inhibiting action of alkalis. If impure iron is kept in $N/10$-sodium hydroxide solution, it will remain unrusted for an indefinite period. Here we have a condition of things which should favour chemical action, namely, the impurities capable of becoming electronegative to the pure metal, and the couple in contact with a conducting solution. How then is the freedom from rust to be explained on the electrolytic theory? It may be that the impurities are destroyed by the alkali, a supposition which is perhaps supported by the observation of Dunstan and Hill that a solution containing less than 0·13 per cent. of sodium carbonate will allow rusting to take place. A more likely hypothesis is suggested by the electrolytic theory. The surface of commercial iron may be regarded as made up of pure iron and impurities such as the sulphide, phosphide, or carbide of iron and free carbon. These are electronegative to pure iron, and would become the cathode when the metal was placed in an alkaline solution. A transient electrolysis would take place, and either or both of two things might happen. The impurities might be coated with hydrogen or the pure metal might receive a superficial coating of oxide. In any case, electrolysis would stop, and the metal would become passive. Dunstan and Hill describe an interesting experiment in which iron is placed in a dilute sodium

[29] *Trans.*, 1908, **93**, 1356. [30] *Science Progress*, 1911, **22**, 311.

chloride solution containing a few drops of phenolphthalein. In absence of air nothing happened, but when air was admitted patches of pink colour appeared on the surface of the metal, rusting taking place on the parts which were not coloured. This is to be explained, not by supposing "a difference of potential set up on the surface of the iron by the action of the air," but by assuming that the polarisation of the cathode is destroyed by oxidation, and that therefore a continuous current can flow and the chemical action proceed. One must regard the question as still an open one, but there can be no question as to the value of the additional experimental evidence which Dunstan and Hill have amassed.

In a recent paper,[30a] Friend states that if iron is kept for some weeks in a 6*N*-solution of sodium or potassium hydroxides, then washed and allowed to remain in distilled water for some hours, it is possible to detect sodium or potassium in the water. He considers that the experiments prove that the metal is porous to the alkaline solution, and that it is the absorbed alkali which induces the apparent passivity of the iron when placed in water. It is to be hoped that the experiments will be repeated, especially as only the exceedingly delicate flame test was used for the detection of the metals. The danger of the adventitious introduction of these metals in small quantities is, of course, well known, and Friend states that in his control experiments none was detected. The writer, after allowing electrolytic iron to remain for a month in solutions of barium hydroxide and sodium hydroxide (2*N* and *N* respectively), and using rigid precautions to exclude dust, was not able to detect the presence of either metal after an exposure of the washed iron to distilled water for five days.

Combustion.

In the Presidential Address[31] Professor H. B. Dixon gave an account of the further series of experiments which he and his collaborators have made on the important question of the ignition-point of an explosive mixture of gases. When the ignition is brought about by the adiabatic compression of the gases by a rapidly moving piston, it is found that before the ignition-point, that is, the point at which rapid self-heating takes place, there is a small amount of chemical combination. By stopping the piston before the ignition-point is reached, and repeating the compression several times, there is, for example, about 1 per cent. of carbon dioxide formed in a mixture of carbon monoxide and oxygen. This combination is called the pre-flame combustion, and it has, by

[30a] *Trans.*, 1912, **101**, 50. [31] *Ibid.*, 1911, **99**, 589.

the heat produced, an influence in bringing the gases up to the ignition-point. In the actual experiments the piston was forced into the glass tube containing the explosive mixture by means of a heavy pendulum allowed to fall from a given height. The piston could be artificially stopped when the ignition-point was reached. Photographs of the explosion were taken on a rapidly moving photographic film. By an ingenious arrangement the duration of the pre-flame period could be determined; it was of the order of 1/100th of a second. With a mixture of carbon monoxide and oxygen the ignition-point was found to be 504°, whilst Falk, who used a similar method, but who allowed his piston to move until it was stopped by the force of the explosion, found 601° for the ignition-point of the same gaseous mixture. It is in the pre-flame period of combustion that Dixon believes the influence of water vapour is exerted, and when the ignition-point has been reached, the action will proceed independently of its action. These researches are of the very highest importance, since it must be by the minute study of the simplest cases of chemical action that, if ever, the nature of chemical attraction will be ascertained.

The study of some cases of combustion from an entirely different point of view has been undertaken by Bloch.[32] Two years ago de Broglie and Brizard[33] showed that the products of combustion of hydrogen and of hydrocarbons were strongly ionised, while the carbon dioxide produced by the burning of carbon monoxide had no conducting power. It seemed that, therefore, there might be some discrimination possible between the character of the chemical action in the one case and the other, which might possibly be correlated with other differences, and that valuable evidence as to the nature of chemical change might be obtained by the study of the ionisation of the products of the change. The results, however, of Bloch lead only to this generalisation, that the flames only of hydrogen and of substances containing hydrogen are accompanied by ionisation; other flames, some of which are hot and some accompanied by little increase of temperature, give rise to no ionisation. Among these are the burning of sulphur in air, sulphur in chlorine, and arsenic in chlorine. Other chemical actions which proceed in the dry way give rise to no ionisation, the combination of hydrogen and sulphur, the combination of sulphur dioxide and oxygen in the presence of spongy platinum, the decomposition of arsine, and the action of zinc on dried hydrogen chloride. It occurred to the writer that it might be possible to connect the five known chemical actions which proceed in the absence of water

[32] *Ann. Chim. Phys.*, 1911, [viii], **23**, 28.
[33] *Compt. rend.*, 1909, **148**, 1596; *A.*, 1909, ii, 637.

vapour with the production of gaseous ionisation. The combustion of carbon disulphide, whether taking place as a "cold" flame, or burning vigorously in a quartz tube, or exploding with violence, produced no conductivity which could be measured by an electrometer. Hence it may be concluded that no connexion can be established between the two phenomena. It is suggested by Bloch that it is possible that the ionisation which has been observed in the combustion of hydrogen-containing substances is connected with the condensation of the water formed and the ionisation produced by the escape of dissolved gases bubbling from the drops. The explanation is a possible one, but it may be that the temperature of these flames being higher than that of the other flames which give no result, there is ionisation produced from the heating of the material of the jet.

The study of the chemistry of explosions in coal mines which is being carried out in a really scientific way at the laboratory established by the Mining Association has produced some papers of great practical, as well as theoretical, importance. The research of Burgess and Wheeler[34] on the lower limit of inflammation of mixtures of the paraffin hydrocarbons with air has, of course, a very direct bearing on mine explosions, and it is also valuable from the scientific point of view. The experiments were performed in a large spherical globe, so as to eliminate as far as possible the influence of the walls of the vessel. Electric sparks were used to ignite the mixtures, the electrodes being arranged in the centre of the globe. It was found that changes in the length of the spark had no influence on the proportions of the gases which would just inflame between the limits of 10 mm. and 50 mm. Small changes in the initial temperature and pressure, such as might take place in a mine, had no measurable influence on the limiting proportions of gas and air. A simple relation between the calorific value and the proportion of combustible gas necessary to form a lower limit mixture was found to hold for five of the simpler paraffin hydrocarbons.

Water of Crystallisation.

The study of the hydration of salts by a dynamical method is the subject of a paper by Partington.[35] His results confirm those of Tammann,[36] and show that the vapour tension of hydrated salts as determined by the dynamic method is always higher than that determined by a static method. The author discusses three possible hypotheses for the explanation of this fact: (1) that it is owing to the incorrectness of the assumption that water vapour obeys the

[34] *Trans.*, 1911, **99**, 2013. [35] *Ibid.*, 1910, **99**, 466.
[36] *Ann. Phys. Chem.*, 1888, [ii], **33**, 329; *A.*, 1888, 403.

gas laws. This he rules out on the ground that the phenomenon appears in the initial stages of a tensimetric measurement. (2) That it is due to the presence of a saturated solution retained on the crystals or occluded in their interior. This the author considers unlikely, since he believes that with the small crystals used the water must, if present at all, have been adherent to the surface of the crystals, and not included. If this were the case the pressures recorded would be higher in the first experiments than in the later ones, whereas the contrary is the case. The author prefers the third hypothesis, which demands the supposition of the existence of an unstable lower hydrate or amorphous salt which slowly passes into a stable, crystalline modification. The work, however, of T. W. Richards[37] shows that included water exists even in the smallest crystals, and nothing short of molecular division would be able to exclude its presence. The second hypothesis seems, therefore, to completely explain the facts, and the supposition of unstable modifications is unnecessary.

Another paper[38] describes work which had for its aim the question whether salts with water of crystallisation could be obtained of sufficiently constant water content to allow of their use for atomic-weight determinations. The work had its origin in the discussion of a paper by Marckwald,[39] who had determined the atomic weight of tellurium by determining the loss in weight of crystallised telluric acid, H_6TeO_6, and from these determinations had concluded that tellurium should occupy its proper place in the periodic table. The authors determined, not only the total loss of weight, but also the water produced when the acid was decomposed. The results showed that in spite of the crystals having been dried for six months over phosphoric oxide, an excess of water over the calculated amount was present, which must have been shut up in the body of the crystal. Investigations were also made to find out if water could pass through a crystal when one face was exposed to a dried atmosphere and the other to a considerable pressure of water vapour. It was found that anhydrous crystals, or those which contained water in chemical combination, such as telluric acid, were impermeable to water vapour, while true hydrates allowed the vapour to pass through them. Crystals were also shown to be impermeable to air at a pressure of an atmosphere. The method used for obtaining the true amount of water of hydration in crystals consisted of (1) the total dehydration of the salt, so as to get rid of adherent as well as of occluded water; (2) the

[37] *Zeitsch. physikal. Chem.*, 1904, **46**, 216.
[38] H. B. Baker and G. H. J. Adlam, *Trans.*, 1911, **99**, 507.
[39] *Ber.*, 1907, **40**, 4370; *A.*, 1908, ii, 33.

re-hydration in an atmosphere containing water vapour, and finally drying over a mixture of the anhydrous and hydrated salt. An interesting point is that the hydrated substance which contains as nearly as possible the true amount of water shows no crystalline form under the microscope.

Rosenstiehl[40] suggests that evidence as to the degree of polymerisation of water can be obtained by observing the manner in which water is driven off from hydrated salts, his idea being that the same relation would hold as regards the complexity of the water molecules in the salts as in the water solution from which they were crystallised. The author hoped to obtain evidence confirming or disproving the present view that ordinary water consists of a mixture of H_2O, $(H_2O)_2$, and $(H_2O)_3$. One hundred and seventy-nine salts were examined, and it was found that salts can be divided into three classes: (1) those containing 1 or 2 and some containing 3 molecules of water. These lose their water at one step. (2) Salts which contain 3, 6, 9, 12, 15, 18, and 24 molecules of water. These salts lose their water in multiples of $3H_2O$. (3) Salts containing 4, 5, 7, 8, and 10 molecules of water. These give results which may indicate that each salt contains two different kinds of water, some containing H_2O and $(H_2O)_2$, and others H_2O and $(H_2O)_3$. There is ingenuity in the idea, but the possibility of the higher polymerides remaining undissociated at the temperature of dehydration is highly problematical.

Metals and Alloys.

The earlier researches in this field of work were largely directed towards the solution of the question as to the mode in which the metals in an alloy were united, whether as a chemical compound, a solid solution, or a eutectic mixture. The field is obviously a very large one, and many chemists regard the investigation of the alloys of any particular pair or triplet of metals with little favour. There is at present a tendency to limit research in this direction to the study of alloys which have some direct use. Dental alloys which contain silver and tin have been investigated by Joyner.[41] In practice these alloys are used as a mercury amalgam, and a remarkable difference has long been noticed as regards the amount of mercury taken up by the filings of the alloy, according as the filings are used at once or kept for some months. The "aged" alloy takes up only about half the mercury which the fresh filings absorb. The "ageing" can be brought about by heating to 100° for half an hour, and according to the author it makes no difference whether the heating takes place in air or in hydrogen. Attempts to

[40] *Bull. Soc. chim.*, 1911, [iv], **9**, 281; *A.*, ii, 386.
[41] *Trans.*, 1911, **99**, 195.

explain the reason of the change in the alloy all failed, although six hypotheses were examined. The author gives no details of the method used to prevent oxidation of the filings during the heating, but he seems to be unaware of the very great ease with which metals can undergo oxidation when ground in an agate mortar.[42] It seems just possible that the "ageing" may be due to a superficial film of oxide. It is demonstrated that at the ordinary temperature there is no solid amalgam of tin, silver, and mercury.

Alloys of aluminium and magnesium, containing only a small proportion of the latter, have been shown [43] to acquire hardness by heating and quenching in cold water. If quenched from 500° in cold water, the metal is at first soft, but the hardness increases in the course of a few days. It was also found that aluminium alloyed with a small quantity of manganese is not wetted by mercury.

A quantitative separation of lead from tin has been effected by distillation [44] in a quartz tube heated in an electric furnace in a mercury-pump vacuum. No trace of tin was carried over, even by heating to a very high temperature. By a special furnace and using a cathode-light vacuum, it was found that the tin could be vaporised in a porcelain tube.

Continuing his researches on the solubility of hydrogen in metals, Sieverts [45] has determined the solubility of this gas in copper, iron, and nickel for pressures up to one and a-half atmospheres and at temperatures between 400° and 1600°. The solubility is independent of the surface of the metal, so that it is due to true solution, and not to adsorption. At constant temperature the solubility in the solid and the fused metals is proportional to the square root of the pressure. At constant pressure the solubility increases with the temperature, and there is a sudden increase in the solubility when the metal melts. The temperature-coefficient is greater with fused than with solid copper. The change from α- to β-iron is not recognisable on the solubility curve, but there is a rapid increase in solubility between 800° and 900°, corresponding with the change from β- to γ-iron. At the respective melting points, as the metals are cooling down, copper gives up 2 volumes, iron 7 volumes, and nickel 12 volumes of the gas, the solidification being accompanied by "spitting."

The occlusion of hydrogen by gold-palladium alloys has been studied by Berry.[46] The method is a delightfully simple one, but

[42] M. C. Carey Lea, *Phil. Mag.*, 1894, [v], **37**, 31.
[43] Wilm, *Metallurgie*, 1911, **8**, 225; *A.*, ii, 493.
[44] Tiede and Fischer, *Ber.*, 1911, **44**, 1711; *A.*, ii, 731.
[45] *Zeitsch. physikal. Chem.*, 1911, **77**, 591; *A.*, ii, 895.
[46] *Trans.*, 1911, **99**, 463.

it seems to be open to two objections. The supersaturation of the hydrogen (stated by Troost and Hautefeuille to be about 30 per cent. of the whole for the pure metal) is assumed to bear a constant relation to the total hydrogen absorbed by the different alloys, and secondly, dilute sulphuric acid was used for the electrolyte. Since palladium is known to be very sensitive to a trace of hydrogen sulphide, and this substance is produced at the cathode in the electrolysis of even very dilute sulphuric acid, it is probable that the results of Hoitzema,[47] as well as those of the author, may be invalidated on this account. In the experiments of Troost and Hautefeuille [48] potassium hydroxide was used as the electrolyte, and since the hydrogen obtained by this method is almost pure, it is probable that their results are the more trustworthy.

Group I.

The study of the behaviour of hydrogen under pressure with solutions of metallic salts has been continued by Ipatieff and Werkhowsky.[49] The authors had shown that the replacement of metal by hydrogen in these circumstances was accompanied by the formation of oxides, hydroxides, and basic salts. It has now been proved that hydrolysis is an important feature in the reaction. At 25 atmospheres pressure and 90°, a $N/10$-solution of copper sulphate gives after fifteen hours a basic sulphate, $CuSO_4,2Cu(HO)_2$; on further treatment this disappears and cuprous oxide is formed, whilst after fifty hours metallic copper makes its appearance. In a later paper [50] Ipatieff has studied the behaviour of copper nitrate and hydrogen under a pressure of 100 atmospheres and at temperatures of 100° to 180°. With $2N$-solutions of copper nitrate it was found that the basic nitrate, $Cu(NO_3)_2,3Cu(HO)_2$, was produced, as well as nitrous acid. If the time was prolonged (one hundred and eighty hours), cupric oxide and copper were formed, and the liquid had an alkaline reaction. With N-solution only traces of the basic nitrate were produced, cuprous oxide and copper being the main products; but the liquid after only twenty-four hours became alkaline. With $2N$-cupric chloride and hydrogen at 100 atmospheres pressure heated to 155° for twenty hours, cuprous chloride was the only solid product, whilst if the $N/5$-solution were used, copper and cuprous chloride were produced. This action was shown to be reversible. Well-defined crystals of nickel were also obtained when $N/5$-nickel chloride solution was heated to 230° with hydrogen at 100 atmospheres pressure.

[47] *Zeitsch. physikal. Chem.*, 1895, **17**, 1; *A.*, 1895, ii, 388.
[48] *Compt. rend.*, 1874, **78**, 968; *A.*, 1874, 660.
[49] *Ber.*, 1911, **44**, 1755; *A.*, ii, 716.
[50] *Ibid.*, 3452; *A.*, 1912, ii, 50.

Continuing his work on the salts and double salts of the alkali metals, Barker[51] has prepared a new periodate of lithium, $LiIO_4,H_2O$; a double rubidium magnesium chromate,

$$Rb_2Mg(CrO_4)_2,6H_2O;$$

and the corresponding salt of cæsium, $Cs_2Mg(CrO_4)_2,6H_2O$. The isolation of the last two salts has rendered it possible to show that the isomorphous relationship which exists between the simple chromates and sulphates also holds for the double salts,

$$R_2Mg[(Cr,S)O_4]_2,6H_2O.$$

The lithium periodate unfortunately is not chemically similar to the periodates of potassium, rubidium, and cæsium,[52] since it crystallises with water. This prevented the testing of the rule, established by the author, that only those members of an isomorphous group of salts which have nearly equal molecular volumes are capable of forming zone crystals or parallel growths on one another. It had been hoped that lithium periodate, if it could have been prepared in the tetragonal anhydrous state, would have formed parallel growths on scheelite ($CaWO_4$), since its molecular volume would presumably be about equal to that of this mineral. It was found, as was to be expected on the author's theory, that no parallel growths are formed on scheelite by the periodates of potassium, rubidium, and cæsium, since their molecular volumes are much greater.

During the last few years a large amount of evidence has been accumulated which tends to show that the chemical activity of some substances in solution bears no relation to the electrical conductivity, and therefore to the ionisation of the solution. It is a pity that this evidence is ignored to a very great extent by the upholders of the dissociation theory. New experiments have been made by Gates[53] on the replacement of metals in non-aqueous solutions. They show that in various organic solvents, such as nitrobenzene, carbon disulphide, carbon tetrachloride, ether, and oleic acid, copper salts of organic acids are soluble, and although the conductivity of these solutions are of the order of 2×10^{-10} mho, copper is deposited by the action of cadmium, lead, zinc, bismuth, magnesium, cobalt, tin, iron, aluminium, silver, antimony, and nickel, the activities of the metals being in the order given. It is noticeable that the order of the metals is quite different from the order of the metals reacting on copper salts in aqueous solutions. Oleic acid, the conductivity of which is less than 2×10^{-10} mho, dissolves sodium, calcium, and potassium at the ordinary temperature, and copper, zinc, lead, and cadmium at 100°.

[51] *Trans.*, 1911, **99**, 1326. [52] Barker, *ibid.*, 1908, **93**, 15.
[53] *J. Physical Chem.*, 1911, **15**, 97; *A.*, ii, 394.

The reaction between hypophosphorous acid and copper sulphate has been examined by Firth and Myers.[54] They confirm the original statement by Wurtz that at 70° the precipitate consists of pure cuprous hydride. After a few minutes' keeping in the liquid the precipitate was found to contain both copper oxide and copper phosphate. The hydride was found to be unstable in the dried state; it could not be kept, even in absence of air, for more than a day.

Group II.

The preparation of peroxides of zinc and cadmium has been effected[55] by the addition of excess of hydrogen peroxide to solutions of the hydroxides of the metals in ammonia. They are said to have the composition $10ZnO_2,4ZnO,5H_2O$; $8ZnO_2,4ZnO,7H_2O$; $5CdO_2,CdO,3H_2O$, and $5CdO_2,3CdO,5H_2O$. They are probably mixtures. The true peroxide of zinc has probably been obtained by Kazanecky[56] by the action of 30 per cent. hydrogen peroxide on potassium or sodium zincoxide. It is white and crystalline, having the composition $ZnO_2.H_2O$, but none of the reactions given distinguishes it from the possible alternative substance, ZnO,H_2O_2.

The problem of the luminosity of the sulphides of the alkaline earth metals after exposure to light is a very attractive one, and but little is known as to the cause of the luminosity. It has been long known that the pure sulphides do not exhibit the phenomenon, and that the luminosity can be very largely increased by the presence of traces of other metals. Vanino and Zumbusch[57] add a further contribution to our knowledge of the subject in showing that polysulphides of the metals must be present for the exhibition of luminosity, but the proportion of the polysulphides needs only to be very small. Vaillant[58] in an attempt to find out the reason of the luminosity has determined the electrical conductivity of the sulphide. The powder was compressed between two conducting surfaces, and the system placed in a circuit with a galvanometer and forty accumulators. The conductivity in the dark being 100, thirty-five minutes' exposure to a 5 c.p. lamp doubled it, and a maximum conductivity of 328 was reached in two hundred and ten minutes. With a 16 c.p. lamp the maximum conductivity of 697 was reached in seventy minutes. On removing the light, the conductivity showed a further increase, and then fell quickly for a few minutes. In the third stage the conductivity decreased

[54] *Trans.*, 1911, **99**, 1329.
[55] Teletoff, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 131; *A.*, ii, 490.
[56] *Ibid.*, 1910, **42**, 1452; *A.*, ii, 282.
[57] *J. pr. Chem.*, 1911, [ii], **84**, 305; *A.*, ii, 885.
[58] *Compt. rend.*, 1911, **152**, 151.

steadily in proportion to the time, and, finally, the decrease was slow and irregular. One cannot fail to be struck with the similarity of these results with the results of similar experiments on the so-called selenium cells, the activity of which, it must be recalled, was shown by Bidwell to be due, not to selenium itself, but to metallic selenides. It has been suggested that the luminosity of the sulphides after exposure to light is due to increased oxidation set up by the illumination. The writer finds, however, that with sulphides which have been sealed up in very pure nitrogen and in as good a vacuum as can be obtained with a mercury pump, the power of becoming luminous is retained unimpaired for three years, during which time traces of oxygen would probably have been absorbed.

Group III.

The existence of the various hydrates of boron trioxide which have been described has been doubtful for a long time. Experiments have now been made [59] which prove that metaboric, pyroboric, and orthoboric acids are the only hydrates which have a real existence, and metaboric and pyroboric acids cannot exist in solution.

A new material which will be of great service to chemists has been made by fusing alumina in the electric furnace. The crystalline oxide is powdered and mixed with some binding substance, and moulded into crucibles, tubes, etc. It bears sudden changes of temperature without cracking, and its melting point is so high that it can be used for melting platinum. The crucibles have one special advantage in being porous, and can be used instead of Gooch crucibles without any asbestos pad. Filtration and washing of precipitates is very rapid, and a Bunsen burner can be applied without preliminary heating to dry the precipitate. A determination of barium by precipitation with sulphuric acid, made in the writer's laboratory, required only twenty minutes, exclusive of the time of cooling in the desiccator and the final weighing of the barium sulphate. The surface of the crucibles is very slightly hygroscopic, but it is possible that this disadvantage may be removed to a great extent by glazing all but the bottom of the crucible.

Group IV.

The behaviour of the diamond at high temperatures has been studied by Doelter.[60] It is found that there is no evidence of the conversion of diamond into graphite when heated in carbon dioxide to 1350°, in hydrogen to 1550°, in nitrogen to 1300°, and in chlorine

[59] Holt, *Mem. Manchester Phil. Soc.*, 1911, **55**, No. 10, 1; *A.*, ii, 720.
[60] *Monatsh.*, 1911, **32**, 275; *A.*, ii, 601.

to 1200°. In some cases only, the diamond darkens in colour, but this is probably due to the presence in the diamond of some occluded impurities. It may be remembered that different specimens of diamond behave very differently when exposed to radium emanation, the one exhibited by Sir William Crookes at the British Association meeting in South Africa having been changed from a pure white to a splendid green, whilst the colours of other diamonds exposed in the same way have been changed to a muddy-brown. Doelter determined the electrical conductivity of the diamond at high temperatures in an atmosphere of nitrogen and hydrogen. The resistance undergoes a remarkable fall from 58,800 ohms at 950° to 370 ohms at 1220°, which increases to 930 ohms at 1260° and falls again to 590 ohms at 1290°.

The interesting series of photochemical researches by D. L. Chapman and his co-workers is continued in a paper on the combination of carbon monoxide and chlorine.[61] Great pains were taken to obtain the gases in a pure condition, but the authors conclude that they were not entirely successful, since there always was an induction period of a short duration on exposing the mixture to light. This period was so short, however, that when one considers the effect of a very minute trace of impurity on the rate of change, the gases must have been of a very high degree of purity. The effect of adding small quantities of oxygen, ozone, nitric oxide, and nitrogen chloride was found to be the same on the rate of reaction of carbon monoxide and chlorine as it is with hydrogen and chlorine. The effect with nitric oxide is very striking. When only 0·3 per cent. of this gas was present, the mixture was exposed to a carbon arc lamp, and the rate of union was found to be extremely slow.

The effect of raising the temperature led to a surprising and what must be considered a very important result, that the rate of combination in the mixture which was heated to 350° was scarcely affected by exposure to light. It was also found that the addition of the gases which were found to inhibit the photochemical change had no effect on the rate of combination brought about by heat. These results distinguish in a way which has never been so clearly demonstrated before, the difference between the effect of heat and light on chemical change.

A paper of considerable interest on the gases adsorbed by the walls of tubes has been published by Guichard.[62] Measuring the gases with a MacLeod gauge, it was found that for 100 sq. cm. surface Jena glass gave off 0·03 c.c. of gas at 600°, porcelain 1·9 c.c.

[61] Chapman and Gee, *Trans.*, 1911, **99**, 1726.
[62] *Compt. rend.*, 1911, **152**, 876; *A.*, ii, 396.

at 1170°, and silica 1·8 c.c. at 1040°. In the last case the gas consisted of carbon monoxide, hydrogen, and carbon dioxide. The results prove how necessary is the preliminary heating of vessels used for very accurate work with highly purified gases.

Kassner stated some years ago that lead monoxide undergoes oxidation in dry air when exposed to sunlight. The experiment has been repeated,[63] and it has been found that if the air is dried by means of phosphoric oxide, no oxidation takes place, even after seven years' exposure.

Group V.

Lobry de Bruyn [64] obtained a crystalline substance by the action of sodium on hydrazine hydrate, to which he assigned the formula $N_2H_5{\cdot}ONa$, ammonia and hydrogen being also produced in the reaction. Scandola,[65] however, working under slightly different conditions, comes to a different conclusion. Hydrazine hydrate was added drop by drop to finely granulated sodium suspended in ether, and the mixture was heated with a reflux condenser on the water-bath. A white substance was produced, which exploded on drying, but which on long contact with ether lost this property. The explosive substance decomposes at 58°, and burns when heated on platinum foil with a slight explosion. It reduces Fehling's solution and ammoniacal silver nitrate. The substance is regarded by the author as a derivative of azoimide.

Hydrazine sulphate is decomposed by liquid ammonia at −33°, giving ammonium sulphate and hydrazine,[66] and by filtering off the former and allowing the ammonia to volatilise, the hydrazine may be obtained.

It has been found that sulphur dissolves in hydrazine and in hydrazine hydrate,[67] giving a dark brown solution, which on pouring into water deposits sulphur. At the ordinary temperature anhydrous hydrazine dissolves 60 per cent. of its weight of sulphur. After a short time nitrogen is evolved, and an unstable hydrosulphide remains in solution. Attempts made to isolate a hydrosulphide by the interaction of hydrogen sulphide and hydrazine resulted in the formation of a crystalline substance, which is probably N_2H_4,H_2S. Sulphur trioxide is at once reduced by hydrazine, sulphur sesquioxide, S_2O_3, being formed.

Rây,[68] in his long and painstaking researches on the nitrites, has

[63] *Arch. Pharm.*, 1911, **249**, 22 ; *A.*, ii, 284.
[64] *Rec. trav. chim.*, 1896, **15**, 174 ; *A.*, 1897, ii, 22.
[65] *Chem. Zentr.*, 1910, ii, 544 ; *A*, ii, 279.
[66] Browne and Welsh, *J. Amer. Chem. Soc.*, 1911, **33**, 1728 ; *A.*, ii, 1084.
[67] F. Ephraim and H. Piotrowski, *Ber.*, 1911, **44**, 386 ; *A.*, ii, 275.
[68] *Trans.*, 1911, **99**, 1012.

studied the effect of adding various nitrates in small quantity to nitric acid while it is allowed to act on mercury. It has been found, whilst the nitrates of sodium, potassium, and manganese have an accelerating effect on the action, ferric nitrate had a distinctly retarding effect. The mechanism of the retarding effect in the last case is not quite clear, but it is undoubtedly connected with the influence of ferric nitrate in preventing to a great extent the formation of nitrous acid. The explanation which seems to the writer as most likely is that the ferric nitrate is reduced to ferrous salt by mercury,[69] and that the ferrous salt inhibits the formation of nitrous acid.[70]

A very similar problem has been investigated by Rennie and Cooke[71] in continuation of their former work.[72] The effect was measured of the addition of small quantities of nitrates of the alkali metals on the rate of solution of copper in nitric acid. It was found that the accelerating or retarding effects of the nitrates of potassium, rubidium, and cæsium were found to be functions of the temperature and of the concentration of the acid.

The monoxide of phosphorus which was prepared by Besson[73] by the interaction of phosphoryl bromide and hydrogen phosphide, on the existence of which as a separate entity some doubts have been cast, has been prepared by Besson and Fournier[74] by passing the silent discharge through a mixture of hydrogen and phosphoryl chloride. The reddish-yellow powder produced has properties identical with those of the oxide previously described.

The complex and much disputed question of the relations of the three phosphoric acids has been investigated by Holt and Myers.[75] It has been shown that pyrophosphoric acid is an intermediate product in the hydration of metaphosphoric to orthophosphoric acid. The result was only obtained qualitatively, since the authors could discover no process for estimating the pyrophosphoric acid in presence of the other two acids. Determinations of the molecular weight of the acids by the freezing-point method pointed to the formula H_3PO_4 for phosphoric acid. For pyrophosphoric acid a sample obtained by the decomposition of lead pyrophosphate by hydrogen sulphide gave also a normal molecular weight, whilst another variety obtained by the dehydration of orthophosphoric acid was probably a mixture of $(H_4P_2O_7)_4$ and $(H_4P_2O_7)_5$. Three

[69] Carnegie, *Trans.*, 1888, **53**, 471.
[70] Veley, *Proc. Roy. Soc.*, 1893, **52**, 27; *A.*, 1893, ii, 413.
[71] *Trans.*, 1911, **99**, 1035.
[72] *Ibid.*, 1908, **93**, 1162.
[73] *Compt. rend.*, 1897, **125**, 1032; *A.*, 1898, ii, 216.
[74] *Ibid.*, 1910, **151**, 876; *A.*, ii, 37.
[75] *Trans.*, 1911, **99**, 384.

specimens of metaphosphoric acid prepared in different ways were examined, and were found to be HPO_3, $(HPO_3)_2$, and $(HPO_3)_3$, the acid prepared from the lead salt being again of simplest formula.

Phosphoric acid has been found[76] to be a useful solvent for certain substances which are only with great difficulty attacked by other reagents. When heated with this acid at 230° for three hours, silicon was dissolved, giving a colourless solution and a gelatinous substance in suspension. Zirconium was dissolved in a few minutes, ferrosilicon, ferrotitanium, titanium nitride, and boron nitride gave clear liquids, and carborundum was entirely decomposed in three hours. Addition of water to the solutions was found to give no precipitate.

Group VI.

It has seemed strange that whilst liquid nitrogen and liquid hydrogen can be easily converted into the solid state by evaporation at diminished pressure, this conversion has not hitherto been effected with oxygen. Sir James Dewar[77] has, however, succeeded in obtaining solid oxygen by evaporating the liquid at the very low pressure obtainable by his cooled charcoal method. The melting-point pressure was found to be as low as 1·11 mm., and even when this was attained solidification did not at once take place, so great is the possibility of supercooling in the liquid oxygen.

A new method for the production of ozone by chemical means has been discovered by Malaquin.[78] When 20 grams of ammonium persulphate mixed with nitric acid are gently heated in an atmosphere of carbon dioxide, ozone is given off, which, purified by passing through dilute alkali, gives a mixture containing 3—4 per cent. of ozone, the rest of the gas being mainly oxygen.

An interesting preparation of concentrated hydrogen peroxide is described by F. Fischer and M. Wolf.[79] The silent discharge was passed through a mixture of hydrogen and oxygen under a pressure of 3 mm., at which pressure the mixture is not explosive, the temperature being maintained at the temperature of liquid air. The yield of hydrogen peroxide in these circumstances is low, but it can be largely increased if the ordinary pressure is used. In this case the explosive mixture must be largely diluted with hydrogen. When 3 per cent. of oxygen and 97 per cent. of hydrogen is used, the yield of hydrogen peroxide was 6·4 at 0·22°, 33 per cent. at −20°,

[76] M. Wunder and B. Janneret, *Compt. rend.*, 1911, **152**, 1770; *A.*, ii, 719.
[77] *Proc. Roy. Soc.*, 1911, A, **85**, 589; *A.*, 1912, ii, 40.
[78] *J. Pharm. Chim.*, 1911, [vii], **3**, 329; *A.*, ii, 387.
[79] *Ber.*, 1911, **44**, 2956; *A.*, ii, 1082.

54 per cent. at −80°, and 87 per cent. at the temperature of liquid air. If oxygen was used to dilute the explosive mixture, ozone was produced, but no hydrogen peroxide.

Sodium hyposulphite has been obtained in concentrated solution by the electrolysis of sodium hydrogen sulphite, using a high current density. Contrary to the opinion generally held, that the salt is decomposed electrolytically, Jellinek [80] has shown that the decomposition is a spontaneous one. The preparation of pure hyposulphite from the commercial product is described in another paper.[81] To a solution in water, sodium chloride is added, and the hyposulphite is precipitated as $Na_2S_2O_4,2H_2O$. This is unstable, but by careful dehydration at 60° the stabler anhydrous salt is formed. It is washed with 50 per cent. alcohol and then with absolute alcohol, and dried in a desiccator at 60°. It can then be kept for months without decomposition. Freezing-point determinations confirm the formula $Na_2S_2O_4$.

A new method of preparing colloidal solutions of selenium is described by Pochettino.[82] Solvents of high boiling points, such as anthracene, phenol, or paraffin, are heated with selenium, and acquire a dark red colour. When solidified, the solution (or suspension) appears red by reflected and blue by transmitted light. Even when heated above the transformation temperature, the red does not pass into the grey selenium. The selenium can be transferred from the solution in which it was prepared to another solvent, for example, from anthracene to carbon disulphide, without change. When platinum plates connected with the poles of a Wimshurst machine are placed in such a solution, the selenium is deposited usually on the positive pole; from a solution in carbon disulphide, however, the selenium is deposited on the negative pole. This is a remarkable development of the most interesting and at the same time most puzzling experiments made by Picton and Linder [83] many years ago.

An unstable telluride of carbon is produced [84] by passing an arc between a tellurium cathode and a graphite anode immersed in carbon disulphide; the solvent acquires a brownish-red colour and an intolerable odour. On cooling the solution to −100°, glistening, brown crystals separate, which re-dissolve when the temperature is allowed to rise. The substance is apparently decomposed when the solution is heated in a sealed vacuous tube at 185°, free carbon and free tellurium being produced. These were separated by

[80] *Zeitsch. Elektrochem.*, 1911, **17**, 245; *A.*, ii, 482.
[81] *Zeitsch. anorg. Chem.*, 1911, **70**, 93; *A.*, ii, 278.
[82] *Atti R. Accad. Lincei*, 1911, [v], **20**, i, 428; *A.*, ii, 597.
[83] *Trans.*, 1897, **71**, 568.
[84] A. Stock and H. Blumenthal, *Ber.*, 1911, **44**, 1832; *A.*, ii, 722.

volatilising the tellurium from the weighed precipitate, and assuming that they were the sole products of the decomposition of the dissolved substance, the formula CTe_2 is indicated for the new compound. The substance has the same unpleasant physiological effects which so many of the compounds of tellurium possess.

No hexahalide derivatives of uranium have hitherto been known, although such compounds of sulphur and chromium are well defined and stable substances. The hexafluoride of uranium has now been isolated by treating the pentachloride with fluorine at $-40°$. The mixture of tetrafluoride and hexafluoride which is obtained is separated by distillation. The hexafluoride is an extremely active substance, attacking glass in presence of moisture, and reacting vigorously with water, alcohol, ether, and benzene. It boils at 56·2°.

Group VII.

Some experiments have been done by Kümmell [85] on the electrical leak between two platinum plates at a difference of potential of 200 volts, which, if confirmed, will be of great importance. When placed in moist or dry hydrogen, nitrogen, carbon dioxide, or oxygen, only a small leak was noticed when the system was exposed to an arc light. In dry chlorine the leak was about the same. When, however, moist chlorine was used, even in the dark, a larger leak was noticed, and this was further increased on exposure to light. Air to which hydrogen chloride had been added was found to give the larger leak. The positively charged platinum cylinder was found to be acted on, but not the plate which was earthed. It should be remembered that Sir J. J. Thomson has shown in a somewhat similar series of experiments that no electrical leak is discoverable when moist hydrogen and chlorine are exposed to light. Experiments in the writer's laboratory similar to those of Kümmell led to contradictory results, the difference of potential used, however, being only 100 volts.

Higgins [86] in a paper on the action of chlorine on alkalis advances some objections to the theory of the action of bleaching powder put forward by Taylor.[87] This theory states that the action of chlorine on alkalis is a reversible one, and that the action of carbon dioxide on solutions of bleaching powder is similar to that of other acids in decomposing both the hypochlorite and chloride present. Taylor showed that the bleaching powder became more active when free alkali was removed or by adding calcium chloride to the solution, provided that no great quantity of free alkali was present.

[85] *Zeitsch. Elektrochem.*, 1911, **17**, 409 ; *A.*, ii, 796.
[86] *Trans.*, 1911, **99**, 858. [87] *Ibid.*, 1910, **97**, 2541.

Higgins bases his objection to the latter statement by some experiments in which lime-water, and lime-water to which calcium chloride had been added, were exposed to air in similar beakers. The calcium carbonate precipitated was weighed, and from the results the conclusion is drawn that there is an increased attraction of the calcium chloride solution for the carbon dioxide of the air. It seems to the writer that no certain conclusion can be drawn from such experiments. The liquids should have been stirred constantly during the whole period to obtain anything like comparable results, especially as the author states that in the pure lime-water the calcium carbonate formed mostly at the surface of the solution, tending to shield the lime-water from the further action of the air. A further paper has been published by Taylor[88] describing some new experiments which strongly support his former conclusions.

Iodine tetroxide has been the subject of a research by Kappeler,[89] who has shown that the various oxides described as being formed by the action of nitric acid on iodine are only iodine tetroxide, I_2O_4. The same substance is also produced by the action of ozonised oxygen on iodine, which Fichter and Röhner[90] considered to be I_2O_9.

A useful method of preparing the anhydrous chlorides of metals has been found by Chauvenet.[91] The oxides are heated to a low red heat in the vapour of carbonyl chloride, and a very good yield is obtained.

Group VIII.

Claude[92] has submitted neon containing only a small quantity of helium to electric discharge between small copper electrodes. The metal volatilises, and on dissolving the sublimed metal in nitric acid it was found to give off eight times as much gas as the same weight of the unvolatilised electrode. The gas from the sublimate was found to contain a large proportion of helium. In repeating the experiment[93] with a tube in the form of a cross with four copper electrodes, the discharge was passed between one pair of the copper surfaces, and then between the second pair. It was found that the sublimate from the first contained much helium, whilst that from the second contained almost pure neon. Instead, therefore, of being a transmutation of neon into helium as appeared at first sight possible, it is only a case of selective absorption of helium in preference to the neon by the metallic copper.

[88] *Trans.*, 1911, **99**, 1906.
[89] *Ber.*, 1911, **44**, 3496; *A.*, 1912, ii, 39.
[90] *Ibid.*, 1909, **42**, 4093; *A.*, ii, 991.
[91] *Compt. rend.*, 1911, **152**, 87; *A.*, ii, 109.
[92] *Ibid.*, 1911, **152**, 1377; *A.*, ii, 602.
[93] *Ibid.*, 1911, **153**, 713; *A.*, ii, 1087.

In order to find out, if possible, if the position of argon, which follows potassium instead of preceding it in the periodic classification, is due to impurity in the argon, F. Fischer and V. Froboese[94] have accomplished the difficult task of fractionally crystallising argon. The melting point of solid argon lies between the boiling point of freshly liquefied air and that which by keeping has lost much of its nitrogen. An apparatus was designed by which the solid and the liquid could be separated at the low temperatures employed. No difference in density, however, was found for the gas which was obtained from the different fractions, and hence the anomalous position of argon, like that of tellurium, still remains unexplained.

H. B. Baker.

[94] *Ber.*, 1911, **44**, 92; *A.*, ii, 202.

ORGANIC CHEMISTRY.

Owing to the enormous number of researches now annually carried out, and to the difficulty in regarding them in true perspective, it is both laborious and perplexing to report on the progress made during a single year in organic chemistry. Rapid as its development is, a review of twelve months in its history gives but a very brief glimpse of the highway of progress, and unless some notable discoveries stand out as guiding marks, it is not easy even to detect the direction taken. Looking back to ascertain whether organic chemistry is moving in alignment with its past or taking a new direction, it seems that recent development might perhaps have been predicted after considering the reports of the last few years.

In these, attention has been several times drawn to the gradual growth among chemists of a conviction that the usual spacial and structural formulæ are in many respects deficient, and of a tendency to seek the aid of dynamic hypotheses and the conception of residual affinity. In the year now under review this tendency has become more marked, and the most interesting recent applications of the conception of residual affinity are those put forward by Emil Fischer and Alfred Werner in discussing the Walden inversion.

Hitherto the theories of residual affinity have been applied in two chief ways, either in justifying the assumption that certain indispensable additive products are formed during a reaction, or in explaining abnormal phenomena as due to the mutual influence of unsaturated atoms in the molecular complex. The explanations offered of the mechanism of the Walden inversion afford an illustration of the former method, whilst Thiele's theory may be quoted as an example of the latter.

Many of those chemists who entertain the view that unsaturated atoms occurring in the same molecular structure may influence the activity of one another, have drawn some support for their contention from anomalies in certain optical properties of substances. This subject has received attention during the past year, the chief workers having as their object the correlation of various physical properties and the study of the influence of various types of

unsaturation. Perhaps one of the more interesting deductions from this line of research is the suggestion that the mutual interference of unsaturated atoms is not confined to cases where these are actually united, but may be found in substances which contain such atoms situated close to one another in space.

The number of elements that can act as the central atoms of molecules in which there is found no plane of symmetry has been extended during the year by the synthesis of optically active compounds of phosphorus, cobalt, and chromium. The possibility of the existence of these active cobalt and chromium compounds had been predicted by Werner's theory of the octahedral structure of compounds containing complexes of the form $[MeA_6]$, and their isolation is valuable evidence of the fundamental correctness of the assumptions underlying his theory of molecular compounds. This theory has been repeatedly shown to be capable of withstanding the severest test to which a theory can be subjected, since it continually leads to predictions which subsequent experiments realise in the most striking manner.

Turning from theory to the more immediate results of experiment, it is seen that very considerable progress has been made in elucidating the constitution of substances occurring in nature. Among the researches attacking these problems from the analytical point of view, a prominent place must be given to those dealing with chlorophyll and hæmatin. The synthetical method continues to be used with great success in work on terpenes and alkaloids.

The growing importance of organic arsenic compounds in the treatment of diseases of protozoal origin is shown by the energy with which their synthesis is being prosecuted, and by the careful protection by patent of every new method and compound. For this reason, as well as on account of their intrinsic interest, they have been dealt with in some detail.

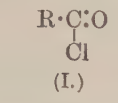
Some Physical Properties.

The greater portion of the work to be reported under this heading has dealt with optical properties, such as refractive and rotatory powers and absorption spectra, and of these perhaps the first-named has occupied most attention. Those engaged in work on the refractivities of organic substances will welcome the careful revision [1] of the atomic constants which appeared at the beginning of the year; the values, being based on more accurate data, replace those formerly calculated by Conrady.

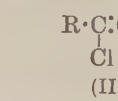
The chief feature of the work with this property is the confirma-

[1] F. Eisenlohr, *Zeitsch. physikal. Chem.*, 1910, **75**, 585; *A.*, ii, 81.

tion and expansion of the rule laid down by Brühl: that the occurrence of unsaturated carbon atoms adjacent to one another causes an anomaly in the refractive and dispersive power of the substance; thus a study of the dioximes [2] has demonstrated that only those which contain the oximino-groups in adjacent positions are anomalous, whilst others in which these groups are separated conform to the additive rule. Brühl's law has been further extended, in a direction indicated by its discoverer, to substances which contain other adjacent elements of unsaturated nature, or those which are capable of existing in higher states of valency.[3] Examples of such elements are the halogens, phosphorus, sulphur, and nitrogen. As might be anticipated, the magnitude of the anomaly varies according to the nature of the other elements to which those in the conjugated system are attached; for example, the acid chlorides (I) exhibit a distinct exaltation, whilst chloro-derivatives of unsaturated hydrocarbons (II) are almost normal:



(I.)



(II.)

In some cases a depression may be set up, and it is shown that this state is not, as previously suspected, confined to heterocyclic compounds, but may be exhibited by widely different classes of substances.

With the aid of the new atomic constants an exhaustive recalculation [4] has been made of the numerical data on which the causal relation between conjugation and anomaly is based. The chief object of this revision seems to have been to trace the effect of substitution in the conjugated system on the magnitude of the exaltation. From the results it is quite clear that substitution tends to reduce the anomaly; but it seems doubtful whether the average values ascribed to various types of conjugated groups can be accepted as accurate. The influence of substitution may be illustrated by the unsaturated ketones:

Type.	E.
·CH:CH·CH:CH·CR:O	3·3
·CH:CR·CH:CH·CR:O	2·7
·CH:CR·CH:CR·CR:O	2·1

Further, it is demonstrated that the position of the substituents as well as their nature influences the magnitude of the anomaly;

[2] F. H. Getman, *Amer. Chem. J.*, 1911, **45**, 539; *A.*, ii, 677.
[3] F. Eisenlohr, *Ber.*, 1911, **44**, 3188; *A.*, 1912, ii, 2.
[4] K. Auwers and F. Eisenlohr, *J. pr. Chem.*, 1911, [ii], **84**, 1, 37; *A.*, ii, 781.

thus in the three types of grouping, where R is a hydrocarbon group:

·C:C·C:C·	·CR:C·C:C	·C:CR·C:C·
(I.)	II.)	(III.)

the first shows the greatest and the last the smallest exaltation; but if substituents containing oxygen are inserted in place of R, the exaltation is much increased.[5] Complex arrangements of conjugated unsaturated groups, such as those usually termed "crossed conjugations," for example:

$$>C{:}C<\begin{matrix}C{:}C<\\C{:}C<\end{matrix} \quad \text{or} \quad >C{:}C<\begin{matrix}C{:}C\cdot\\C{:}O\end{matrix},$$

uniformly lead to enhanced exaltation.

Other work which is probably of more general interest to the chemist has been undertaken[6] in the study of the relations between optical anomaly and chemical reactivity. By comparing derivatives of ethylenediamine with similar derivatives of piperazine, for example:

$$C_5H_{10}N<\begin{matrix}CH_3 & CH_3\\CH_2—&—CH_2\end{matrix}>NC_5H_{10} \text{ with } C_5H_{10}N<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>NC_5H_{10},$$

it is found that on forming the cyclic system the reactivity of the nitrogen atoms is increased, and this increase in chemical activity is accompanied by an exaltation of refractive power, the open-chain compound being optically normal. It is thus clear that the formerly accepted rule that ring formation is without effect on refractive power does not always hold, and it is suggested that this condition is here due to the conjugation of the unsaturated nitrogen atoms by virtue of their proximity in space. It is interesting to notice that the evidence for this type of conjugation, or "space conjugation" as it is termed, has obtained support[7] from another physical property.

From this very brief account of recent research in the subject it is evident that the additive laws laid down by the pioneers of the work are becoming narrowed in their scope, and are being replaced by other more numerous sets of additive relations. No doubt at some future date the latter will, in their turn, be superseded.

Other investigations have dealt with the influence of unsaturated groups on the general absorptive power of substances. This work[8]

[5] K. Auwers, *Ber.*, 1911, **44**, 3514; *A.*, 1912, ii, 3. See, however, Miss I. Smedley, *Trans.*, 1910, **97**, 1475, 1484.

[6] H. T. Clarke, *Trans.*, 1911, **99**, 1432.

[7] T. P. Hilditch, *ibid.*, 1909, **95**, 1578.

[8] C. R. Crymble, A. W. Stewart, R. Wright, and W. G. Glendinning, *ibid.*, 1911, **99**, 451.

has shown that ethylenic compounds exert greater general absorption than the corresponding saturated derivatives; but if conjugation of the unsaturated groups occurs, there is a marked increase in absorption. In other respects, however, the relations of this property to unsaturation differ from those found with refractive power, for systems containing the crossed conjugation exhibit a diminished absorptive effect. With simple compounds containing iodine it has been observed that a characteristic absorption band is developed when two or more atoms of that element are brought together, as in methylene iodide and iodoform[9]; and this effect is evidently due to some influence analogous to conjugation. It appears also probable that a similar relation may hold with compounds of sulphur. This element,[10] under certain conditions such as those occurring in the group $>C{:}S$, may function as part of a chromophore, and in many cases its absorptive effect is greater than that of oxygen.

Other very interesting researches on the relation between absorptive power and the constitution of derivatives of ketopentamethylene have been made[11]; but nothing more can be done in this place than to draw attention to these and to others[12] conducted with vapours of simple benzenoid compounds, with hydrazones of camphorquinone,[13] and with nitro-derivatives of dimethyltoluidine.[14]

Researches conducted with optically active compounds have shown that the property is influenced by the presence of unsaturated groups and by their relative situation. In studying a property of such highly constitutive nature as this, it is difficult even approximately to eliminate all disturbing factors, and it is thus impossible to state any general rule[15] as to the relative influence of the ethylenic and acetylenic systems. Nevertheless, it has been made clear that the conjugation of unsaturated groups has a distinct influence[16] on optical activity, but it is interesting to notice that the magnitude of the anomaly depends on the relative situations of the asymmetric and conjugated systems, as well as on other external factors such as the solvent. The general study[17] of the influence of the solvent has an important bearing

[9] C. R. Crymble, A. W. Stewart, and R. Wright, *Ber.*, 1910, **43**, 1183, 1188, 1191; *A.*, ii, 470; *ibid.*, 1911, **44**, 2819; *A.*, ii, 1043.

[10] J. E. Purvis, H. O. Jones, and H. S. Tasker, *Trans.*, 1910, **97**, 2297.

[11] J. E. Purvis, *ibid.*, 1911, **99**, 107, 1953.

[12] J. E. Purvis, *ibid.*, 811, 1699.

[13] F. R. Lankshear and A. Lapworth, *ibid.*, 1785.

[14] G. T. Morgan and A. Clayton, *ibid.*, 1941.

[15] P. F. Frankland and H. H. O'Sullivan, *ibid.*, 2325; T. P. Hilditch, *ibid.*, 218.

[16] T. P. Hilditch, *ibid.*, 224.

[17] T. S. Patterson and Miss E. F. Stevenson, *ibid.*, 1910, **97**, 2110; E. C. C. Baly, *Zeitsch. Elektrochem.*, 1911, **17**, 211; *A.*, ii, 451.

on this question, whilst other researches with liquids have been undertaken in order to elucidate[18] the finer influences of constitution on the property. From the data obtained with alcohols containing a single asymmetric carbon atom it has been found that in the homologous series the rotation tends to reach a limiting value.

Within the two past years magnetic susceptibility has been added[19] to the list of physical properties recommended as an aid to the study of constitution in organic substances. The additive and constitutive features of magnetic susceptibility are fairly evenly balanced, although the property is undoubtedly more sensitive than refractive power to the influence of constitution, and in general character it may be placed at about a level with magnetic rotation. It has been shown that the molecular magnetic susceptibility may be represented by the sum of certain atomic values, but the latter vary according to the mode of saturation of the atoms, and a further allowance in the summation must be made for the general structure of the molecule. Nevertheless, if these conditions are taken into account, the calculation of molecular value may be performed with considerable accuracy.

The application of the method to determining the constitution of benzene does not give decisive results in favour of any of the usual formulæ, but if any definite conclusion may be drawn from the data, it seems that the "centric" formula must be chosen. The magnetic susceptibilities of compounds containing the keto-methylene group have also been measured, and in many instances the data point to the presence of the enolic isomeride. It is noteworthy that according to this method freshly prepared acetoacetic ester would contain about 70 per cent. and the equilibrium mixture about 17 per cent. of the enolic form. As preliminary results, these are interesting, but since they are at variance with those given by chemical methods[20] and by other physical data, it seems that further research is necessary before the property can be applied with confidence to problems of this nature.

Polymorphism and Isomerism.

The terms polymorphism (including, of course, di-, tri-, and tetramorphism, etc.) and isomerism have been long in use in connexion with phenomena of an extremely fundamental character, and it is

[18] R. H. Pickard and J. Kenyon, *Trans.*, 1911, **99**, 45.

[19] P. Pascal, *Bull. Soc. chim.*, 1909, [iv], **5**, 1110; 1910, [iv], **7**, 17, 45; 1911, [iv], **9**, 6, 79, 134, 177, 336, 809, 868; *Compt. rend.*, 1910, **150**, 1167; 1911, **152**, 862; *A.*, 1910, ii, 100, 179, 580; 1911, ii, 91, 183, 251, 252, 464, 850.

[20] See later.

therefore of the utmost importance to have a correct understanding of the connotation implied. Suppose a substance of a given chemical composition appears in more than one crystalline form: when this is attributable, not to differences within the chemical molecule, but to a difference in the manner in which the molecules as a whole mutually arrange themselves during the act of crystallisation, we are dealing with a polymorphous substance. It is evident that the polymorphous appearance is wholly bound up with the crystalline (solid) state; when this condition is lost either by melting, dissolving, or vaporising, all differences disappear. If, on the other hand, the different forms are due to differences *within* the chemical molecule, they can also persist in the liquid, dissolved, or gaseous states, and the forms must be regarded as isomeric. It is seen that polymorphism and isomerism exhaust all the theoretical possibilities. There would seem to be an opinion, however, in many quarters that the two terms merge into one another, and there is a tendency to explain certain cases as lying on the border line. The non-existence of such a border line has been recently emphasised in an able paper by Biilmann.[21] Substances are to be regarded as polymorphous provided that in no circumstances are properties exhibited which are not explicable by a single chemical formula. Great hesitation should therefore be exercised before designating two forms as isomeric, unless one is finally forced to that assumption by direct observations resulting from a study either of chemical actions or of such physical properties as have been proved to be of a constitutive nature. It may be added that Biilmann's work on the two modifications of picrylphenylmethylamine, formerly studied by Hantzsch,[22] and considered by him to be "homochromoisomeric" (see below), makes it extremely probable that they constitute an ordinary case of dimorphism. The same would also seem to apply to many of Hantzsch's chromoisomeric compounds, but further work is necessary before a final decision can be arrived at. Another example in which two forms have been for long regarded as isomeric, whilst more recent research points to dimorphism, is the much discussed case of the cinnamic acids. Stobbe[23] has made an exceedingly careful study of the mutual transformations of *allo-* (m. p. 68°) and the two *iso-* (m. p. 42° and 58°) cinnamic acids. Extreme care was taken to avoid accidental seeding, as is proved by the concordant results obtained. By melting either of the three acids, identical fusions are obtained, the identity being

[21] E. Biilmann, *Ber.*, 1911, **44**, 827; *A.*, i, 367.
[22] A. Hantzsch, *ibid.*, 1910, **43**, 1651; *Ann. Report*, 1910, 78.
[23] H. Stobbe, *Ber.*, 1911, **44**, 2739; *A.*, i, 859.

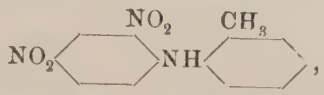
proved optically by Stobbe and Reuss,[24] and the introduction of a crystal fragment of any particular modification into the supercooled fusion always leads to a complete solidification into that modification. In this way, then, any one of the three acids can be transformed into either of the other two. Transformation of the two *iso*- into the *allo*-acid may also be effected by inoculation without previous melting, the progress of the transformation being visible in a melting-point tube by the growing opacity of the clear crystals, or under the polarising microscope by the change of interference tint. The 42° acid may be directly transformed into the 68° acid, or indirectly by changing into the 58° with a subsequent transformation, but the reverse change cannot be effected (without melting), so that the 68° acid may be regarded as stable, the 58° metastable, and the 42° labile. These results are not contrary to expectation, but the further observation that the velocity of transformation of the *iso*-acids into the *allo*-acid is extraordinarily increased by lowering the temperature to $-80°$ or $-180°$ is very remarkable. It is, however, perhaps not in opposition to theory, for Kruyt[25] shows that the maximum velocity of transformation may well obtain at low temperatures, for it will depend, not only on the number of crystallisation nuclei, but also on their rate of growth, and these two factors when taken together may yield the highest result at low temperatures. A somewhat similar existence and mutual transformation are met with in the tetramorphous chloroacetic acid, in which there is no possibility of chemical isomerism; hence Stobbe draws the conclusion that all three forms of cinnamic acid are to be regarded as polymorphous forms of the trimorphous *cis*-cinnamic acid, $\begin{matrix} C_6H_5\cdot C\cdot H \\ CO_2H\cdot C\cdot H \end{matrix}$. Although this work does not, perhaps, altogether close the question of the constitution of the cinnamic acids, it certainly is an indication that the number of structurally isomeric cinnamic acids is by no means greater than the two allowed by geometrical theory.

Chromoisomerism and *Homochromoisomerism*.—These two terms have been proposed and employed for some years by Hantzsch to connotate the appearance of substances in more than one solid modification: "Chromoisomerides are those which are characterised by similar, or only slightly dissimilar, behaviour in the chemical sense, but which differ from each other in colour, and hence have a different light absorption; homochromoisomerides are distinguished from the former in that they possess the same colour and identical absorption spectra, molecular extinction, and refrac-

[24] H. Stobbe and F. Reuss, *Ber.*, 1911, **44**, 2735; *A.*, i, 859.
[25] H. R. Kruyt, *ibid.*, 3108; *A.*, i, 975.

tion." As examples of homochromoisomerides, Hantzsch cites certain nitroanilines, stereoisomeric oximes, and coloured salts of dinitro-compounds.

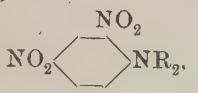
The results of Hantzsch's former work in this field of research, which related chiefly to the nitrophenols and nitroanilines, were described in last year's report (p. 78). In the nitroaniline series the case of 2:4-dinitrophenyl-*o*-tolylamine,



is especially noteworthy, as it exists in four different solid modifications, two being orange and two yellow. Now Hantzsch himself admits that all the four forms, as indeed is general with all chromoisomerides, yield optically identical solutions; they also yield the same derivatives. Since, then, the difference is restricted to the solid form, it does not seem necessary to postulate isomerism at all, but merely polymorphism. It may be remarked that polymorphous modifications are not invariably of the same colour, and in those cases where the colour is the same the shade is appreciably different.

A close perusal of Hantzsch's papers certainly gives the impression that the great majority of chromoisomerides are in reality polymorphous modifications; at any rate, the evidence in favour of polymorphism as opposed to isomerism is overwhelmingly preponderant. Hantzsch avers that polymorphism is out of the question, since solutions of certain chromoisomerides in different media are of quite a different colour; and since the solute is always found to be unimolecular, it can be assumed that the difference in colour of the solution is due to the presence of different chromoisomerides. In a later paper, however, Hantzsch recognises the possibility, and even regards it as likely, that the difference in colour is due to the formation of "solvates," that is, compounds of solvent and solute.

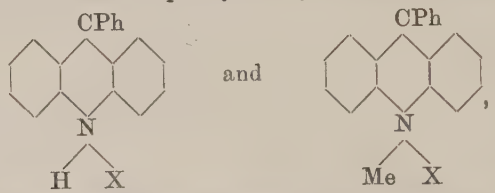
As mentioned previously, the chromoisomerism in the nitroaniline series is only evident in the solid condition, all differences disappearing on solution, and in order to prove the existence of isomerism Hantzsch is therefore restricted to a comparison of the physical properties of certain homologous series; thus the members of the homologous series,



where R is methyl, ethyl, or propyl, all dissolve in chloroform, yielding yellow solutions, and the increments in molecular refraction on replacing methyl by ethyl, and ethyl by propyl are

respectively 9·5 and 9·4—values which are in close agreement with the theoretical value 9·2 (Brühl). On the other hand, in the corresponding 3 : 4-dinitroanilines, the solutions in pyridine of the dimethyl and diethyl compounds are respectively yellow and orange, and the observed increment is only 7·8 instead of 9·2. From this Hantzsch draws the conclusion that the pair of substances cannot belong to an homologous series, but to two different isomeric series, and hence the difference of colour is due to isomerism. It seems plausible to suggest, however, that the anomalous result, which indeed is beyond the range of experimental error, may be due to the formation in solution of different amounts of the additive compound of solvent and solute, for pyridine is strongly basic and the nitroanilines are slightly acidic.

During the current year Hantzsch [26] has considerably extended his observations, and has prepared a large series of chromoisomeric derivatives in the pyridine, quinoline, and acridine series. Of these, by far the most numerous and stable forms are afforded by the phenylacridonium and phenylmethylacridonium salts:



Phenylacridonium hydrogen sulphate, for example, exists in three forms—yellow, red, and green—whilst phenylmethylacridonium sulphite yields four forms—yellow, red, green, and brown. With all the new derivatives the solutions obtained from the variously coloured modifications are identical; but the colour of the solution depends greatly on the solvent used, as is evident from the following table relating to phenylmethylacridonium sulphite:

Ethyl alcohol.			Glacial acetic acid.	Acetylene di- and tetra-chloride.	Aceto-nitrile.	Nitro-methane.	Nitro-benzene.
Absolute.	Moist.	Amyl alcohol.					
Red	Greenish-yellow	Greenish-brown	Red	Green	Golden-yellow	Yellowish-brown	Brown

The difference of colour in different solvents Hantzsch attributes, not to association or polymerisation, but to the formation in solution of solvates. With respect to the number of chromoisomerides, Hantzsch is of the opinion that there are three, namely, yellow, green, and red, all the other coloured varieties being regarded as due to equilibrium mixtures of these three in different proportions. Phenylacridonium sulphate yields only the three pure

[26] A. Hantzsch, *Ber.*, 1910, **44**, 1783; *A.*, i, 673.

isomerides, but phenylmethylacridonium sulphite yields in addition the dark brown salt, which is to be regarded as a mixture of the green and red salts, for on contact with ether it gives the ether-stable green salt, whereas with chloroform the red salt is obtained.

Formulation of Chromoisomerides.—The view formerly held, that this isomerism is due to polymerism or association, is now given up by Hantzsch, in favour of an application of Werner's theory of valency isomerism. As is well known, according to this theory in the formation of an ammonium salt the acidic and basic parts of the molecule are held together by their auxiliary valencies or residual affinities:

$$H_3N + HCl \longrightarrow H_3N \ldots HCl.$$

Now in the parent ammonium salts, NH_4X, there is no possibility of isomerism, but with $NR_3R'X$ we have two possibilities:

$$R_3{:}N \ldots R'X \quad \text{and} \quad R_2R'{:}N \ldots RX,$$

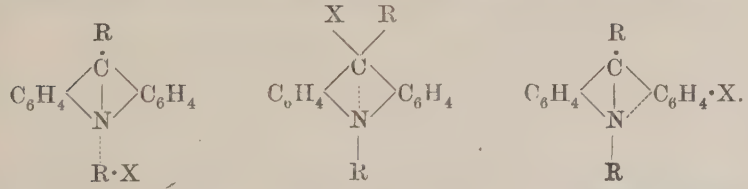
and the greater the difference in character between R and R′ the more likely are the two to possess stable individuality. This would especially hold good for the pyridonium and other bases, because in them the anion would be united either to H (or CH_3) or to the unsaturated carbon ring:

$$\underset{\text{(I.)}}{C_5H_5N \ldots CH_3X} \qquad \underset{\text{(II.)}}{X \cdot C_5H_5N \cdot CH_3};$$

by addition of methyl iodide to pyridine we should get the two forms:

$$C_5H_5N \cdot CH_3I \quad \text{or} \quad C_5H_5{:}N \ldots CH_3I,$$
$$I \cdot C_5H_5N \cdot CH_3 \quad \text{or} \quad I \cdot C_5H_5 \ldots N \cdot CH_3.$$

In the acridine series there is a particularly good agreement between the number of isomerides theoretically possible and those found:



These three formulæ correspond with the three chromoisomeric forms—yellow, green, and red.

Hantzsch's work has furnished organic chemistry with a number of new compounds, which exist in two or even more differently coloured modifications, but his conclusions seem to be more far-reaching than the experimental evidence warrants. It is much to be regretted that in the examination of the supposed isomerides Hantzsch has not employed any crystallographic methods; in some cases, it is true, determinations of melting point were made, but in

others the only property employed for discrimination between supposedly different modifications was colour, and this is perhaps more than any other affected by slight impurity.

Stereochemistry.

The Walden Inversion.

Some sixteen years ago Walden,[27] who was then investigating the optically active modifications of halogen substituted succinic acids, was led to the wholly unexpected conclusion that in certain reactions it is possible to convert an active compound containing an asymmetric carbon atom into its enantiomeride, without previously racemising it and then resolving the racemic compound.

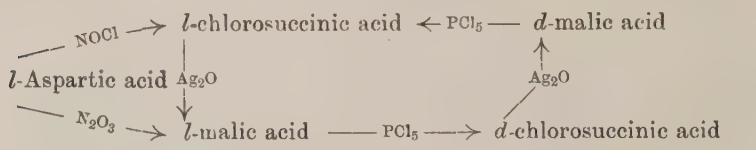
Phenomena of this character, which have been grouped together by Emil Fischer[28] under the designation "The Walden Inversion," although among the most surprising discovered in connexion with optically active substances, have up to the present time found no generally accepted theoretical explanation.

The results as yet obtained may be appropriately summarised here, as several explanations have been put forward during the past year to account for them.

They all relate to changes in which halogen, hydroxy-, and amino-acids are converted the one into the other.

As is well known,[29] aspartic acid, $CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO_2H$, can be converted into malic acid, $CO_2H{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H$, by nitrous acid, and into chlorosuccinic acid, $CO_2H{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2H$, by nitrosyl chloride. Again the action of silver oxide converts chlorosuccinic acid into malic acid, whilst phosphorus pentachloride effects the reverse change.

Walden found that if these reactions are carried out with optically active material, compounds are obtained the signs of rotation of which are represented in the following scheme:



[27] P. Walden, *Ber.*, 1895, **28**, 1287 ; *ibid.*, 1896, **29**, 133 ; *ibid.*, 1897, **30**, 3146 ; *ibid.*, 1899, **32**, 1833, 1855 ; P. Walden and O. Lutz, *ibid.*, 1897, **30**, 2795.

[28] E. Fischer, *ibid.*, 1906, **39**, 2895.

[29] Compare Piria, *Annalen*, 1848, **68**, 349 ; Pasteur, *Ann. Chim. Phys.*, 1852, [iii], **34**, 46 ; Piutti, *Ber.*, 1886, **19**, 1693 ; Tilden and Marshall, *Trans.*, 1895, **67**, 494.

Not only lævorotatory, but also dextrorotatory, chlorosuccinic acid can thus be obtained from one and the same lævorotatory aspartic acid, according as the amino-group is replaced by chlorine by means of nitrosyl chloride, or is first replaced by hydroxyl by means of nitrous acid, the hydroxyl being subsequently replaced by chlorine with the aid of phosphorus pentachloride. Further, lævorotatory or dextrorotatory chlorosuccinic acid can be converted each into its enantiomeride on replacing the chlorine atom by a hydroxyl group through the agency of silver oxide, and then re-introducing the chlorine in place of the hydroxyl group by means of phosphorus pentachloride. An optical cycle of changes is thus accomplished, during which a change of configuration occurs.

As simple derivatives of optically active compounds, in the formation of which no change of configuration is likely to have taken place, frequently show a sign of rotation opposite to that of the parent compound, it cannot be decided offhand at which stage of the process: action of phosphorus pentachloride or action of silver oxide, change of configuration occurs, and much work has been done in attempts to decide this point.

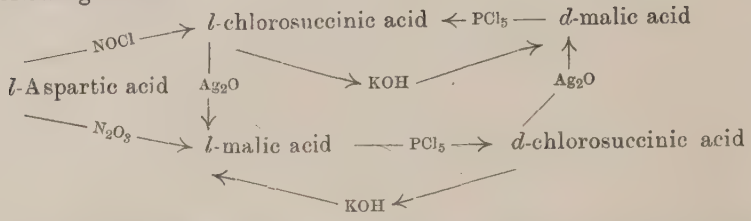
Walden showed that different enantiomerides of malic acid could be obtained from the chlorosuccinic acids by simply altering the reagent by which the replacement of hydroxyl was effected, for whilst either dextro- or lævo-rotatory chlorosuccinic acid when acted on by silver oxide yields a malic acid of the same sign, it is converted by potassium hydroxide into a malic acid of the opposite sign, thus:

l-Chlorosuccinic acid	$+Ag_2O$	$\longrightarrow$	*l*-malic acid
	$+KOH$	$\longrightarrow$	*d*-malic acid
d-Chlorosuccinic acid	$+Ag_2O$	$\longrightarrow$	*d*-malic acid
	$+KOH$	$\longrightarrow$	*l*-malic acid

On the ground of prevailing views on the nature of solution, Walden drew the conclusion that in these reactions probably phosphorus pentachloride and potassium hydroxide act optically normally, that is, act without altering the configuration, but that the reverse is to be assumed for silver oxide.

He found that although exceptions occur, as a rule strong bases cause a reversal of the rotatory power, whilst feeble bases give a malic acid of similar sign, and suggested that the formation of the different optical isomerides was possibly due to one being produced by direct substitution of hydroxyl for halogen by the interaction of ions, and the other by the intermediate formation of an additive compound of the base and the acid.

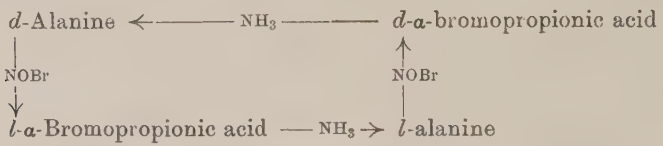
The position reached by Walden can be summarised in the following scheme:



In all such optical cycles atoms or groups must obviously play a part, which, in the equations ordinarily used to represent the reactions, are not shown to be concerned. Similar changes of configuration have been long known to occur during racemisation, but these find a limit in a state of equilibrium characterised by inactivity due to the presence of equal amounts of each active form.

In the changes investigated by Walden an acid distinguished by an entirely reversed direction of rotation is obtained.

Some years later Emil Fischer[30] was led to the subject in the course of his work on the amino-acids, and discovered that a similar reversal of rotatory power is effected when the latter are converted into the bromo-acids and these are reconverted into the amino-acids by the action of ammonia. He showed that, as a rule, a cyclic series of reactions could be carried out, which may be represented, for example, by the scheme:



and noted that the change of configuration might take place either during the action of the nitrosyl bromide or of the ammonia.

It is seen from the above scheme that when the halogen of an active α-bromopropionic acid is replaced by an amino-group,[31] an alanine of similar rotatory power is obtained. Fischer found that this is the case when either the free acid or its ester is employed, but that working in the opposite direction and changing an active alanine into an active α-bromopropionic acid by means of nitrosyl bromide, the direction of rotation of the halogen acid produced is

[30] E. Fischer, *Ber.*, 1907, **40**, 489; *A.*, 1907, i, 192.

[31] It may be noted that in the case of the *d*-bromo-fatty acids this replacement can be carried out very easily, whilst Walden was unable to effect a similar replacement of halogen by an amino-group in the halogen substituted succinic acids.

different according as free alanine or its ethyl ester is employed, in the latter case the product being subsequently hydrolysed, thus:

$$d\text{-Alanine } (NH_2\cdot CHMe\cdot CO_2H) \xrightarrow{NOBr} l\text{-}\alpha\text{-bromopropionic acid.}$$

$$d\text{-Alanine ester } (NH_2\cdot CHMe\cdot CO_2Et) \xrightarrow[\text{hydrolysis}]{\text{NOBr and}} d\text{-}\alpha\text{-bromopropionic acid.}$$

In one case or the other, therefore, change of configuration must have been brought about, and Fischer consequently thought it probable that optical inversion in the compounds studied by him was caused by nitrosyl chloride or bromide, that is, its action was sterically abnormal, whilst the replacement of bromine by the amino-group through the agency of ammonia was sterically normal, and that therefore *d*- and *l*-alanine correspond in configuration with *d*- and *l*-α-bromopropionic acid respectively.

Similar differences of behaviour between amino-acids and their esters have been observed in other cases,[32] but an exception is found in α-amino*iso*valeric acid, $CHMe_2\cdot CH(NH_2)\cdot CO_2H$, or valine,[33] as it is called.

The α-bromo*iso*valeric acid obtained by the action of nitrosyl bromide on *l*-valine gives again the original *l*-valine when acted on by ammonia, thus:

$$l\text{-Valine} \underset{NH_3}{\overset{NOBr}{\rightleftharpoons}} d\text{-}\alpha\text{-bromo}iso\text{valeric acid.}$$

Further investigation, however, has increased the number of instances where slight alterations in the groups attached to the asymmetric carbon atom cause reactions to proceed in optically different manners.

Fischer,[34] for example, found that the products obtained from the α-halogen fatty acids by the action of silver oxide were optically different, according as the silver oxide was made to act on the free halogen fatty acid or the product obtained by coupling its acid chloride with glycine; thus, whilst *l*-α-bromopropionic acid yields *l*-lactic acid, *d*-lactic acid is obtained by hydrolysis of the product obtained from *l*-α-bromopropionylglycine:

$$l\text{-}CHMeBr\cdot CO_2H \xrightarrow{Ag_2O} d\text{-}OH\cdot CHMe\cdot CO_2H.$$

$$l\text{-}CHMeBr\cdot CO\cdot NH\cdot CH_2\cdot CO_2H \xrightarrow[\text{hydrolysis}]{Ag_2O \text{ and}} l\text{-}OH\cdot CHMe\cdot CO_2H.$$

Again,[35] the action of ammonia on derivatives of the α-halogen fatty acids, although in most cases it yields products of the same

[32] E. Fischer, *Ber.*, 1907, **40**, 502; *A.*, 1907, i, 192; E. Fischer and K. Raske, *Ber.*, 1907, **40**, 1052; *A.*, 1907, i, 381; E. Fischer and W. Schoeller, *Annalen*, 1907, **357**, 11; *A.*, 1907, i, 1037.

[33] E. Fischer and H. Scheibler, *Ber.*, 1908, **41**, 889; *A.*, 1908, i, 324.

[34] Fischer, *Ber.*, 1907, **40**, 494; *A.*, 1907, i, 192.

[35] E. Fischer and H. Scheibler, *Ber.*, 1908, **41**, 889, 2891; *A.*, 1908, i, 324, 857.

sign, whether the free acids or their esters or their combinations with glycine are employed, yet gives optically different α-amino-*iso*valeric acids when *d*-α-bromo*iso*valeric acid,

$$CHMe_2\cdot CHBr\cdot CO_2H,$$

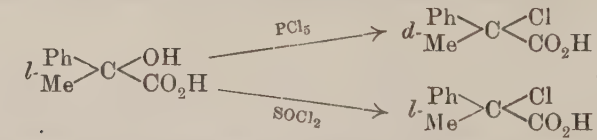
and *d*-α-bromo*iso*valerylglycine, $CHMe_2\cdot CHBr\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, are employed, thus:

d-α-Bromo*iso*valeric acid $\xrightarrow{-NH_3}$ *l*-valine.

d-α-Bromo*iso*valerylglycine $\xrightarrow{-NH_3 \text{ and hydrolysis}}$ *d*-valine.

The fact that change of configuration does not necessarily accompany any particular reaction, but that the reagent effecting it plays an important part, was first established by Walden when he discovered that *d*-malic acid is produced when the halogen of *d*-chlorosuccinic acid is replaced by hydroxyl through the agency of silver oxide, whilst *l*-malic acid results when potassium hydroxide is employed.

Other instances have since been discovered, for example,[36] *l*-α-hydroxy-α-phenylpropionic acid or its ester is converted by phosphorus pentachloride into the corresponding *d*-chloro-acid, and by thionyl chloride into the corresponding *l*-acid, thus:



Most cases of the Walden inversion have been observed in transformations of α-substituted acids and their derivatives, which are much more readily obtained and react more easily than the corresponding β-derivatives, and it at first appeared that the inversion could not be effected where the carboxyl group was not directly attached to the asymmetric carbon atom; for example, no reversal of the configuration was shown in the following transformations[37]:

$$l\text{-}OH\cdot CHMe\cdot CH_2\cdot CO_2H \underset{Ag_2O \text{ or water}}{\overset{PCl_5}{\rightleftharpoons}} d\text{-}CHMeCl\cdot CH_2\cdot CO_2H$$

and

$$l\text{-}OH\cdot CHPh\cdot CH_2\cdot CO_2H \underset{Ag_2O \text{ or water or } Na_2CO_3}{\overset{HBr \text{ or } PBr_5}{\rightleftharpoons}} d\text{-}CHPhBr\cdot CH_2\cdot CO_2H$$

and

$$d\text{-}NH_2\cdot CHPh\cdot CH_2\cdot CO_2H \xrightarrow{-HNO_2} l\text{-}OH\cdot CHPh\cdot CH_2\cdot CO_2H,$$

$$d\text{-}NH_2\cdot CHPh\cdot CH_2\cdot CO_2Et \xrightarrow{-HNO_2} l\text{-}OH\cdot CHPh\cdot CH_2\cdot CO_2Et.$$

[36] A. McKenzie and G. W. Clough, *Trans.*, 1910, **97**, 1016, 2566.

[37] E. Fischer and H. Scheibler, *Ber.*, 1909, **42**, 1219; *A.*, 1909, i, 359; A. McKenzie and H. B. P. Humphries, *Trans.*, 1910, **97**, 121; E. Fischer, H. Scheibler, and R. Groh, *Ber.*, 1910, **43**, 2020; *A.*, 1910, i, 672.

It has, however, recently been shown [38] that each of the active β-aminobutyric acids [39] can be converted into either of the two optically opposed active β-hydroxybutyric acids, according as the conversion is effected by using nitrous acid, or by first employing nitrosyl chloride and afterwards heating the resulting β-chlorobutyric acid with water; thus, for example:

$$d\text{-}NH_2\cdot CHMe\cdot CH_2\cdot CO_2H \xrightarrow{HNO_2} l\text{-}OH\cdot CHMe\cdot CH_2\cdot CO_2H$$

$$\downarrow NOCl$$

$$l\text{-}CHMeCl\cdot CH_2\cdot CO_2H \xrightarrow{H_2O} d\text{-}OH\cdot CHMe\cdot CH_2\cdot CO_2H$$

From this it follows that at least in one of the reactions employed a change of configuration takes place, and the phenomenon is therefore no longer limited to the α-substituted acids.

This conclusion has been lately confirmed by the optical inversion of the active β-hydroxy-β-phenylpropionic acids by means of thionyl chloride, which is found to act differently from hydrochloric acid and phosphorus pentachloride.

The interconversion of the hydroxy-acids was realised [40] in accordance with the following scheme, which therefore represents the first optical cycle actually carried through with the β-hydroxy-acids:

$$d\text{-}OH\cdot CHPh\cdot CH_2\cdot CO_2H \xrightarrow{SOCl_2} d\text{-}CHPhCl\cdot CH_2\cdot CO_2H$$

$$\uparrow H_2O \qquad\qquad \downarrow H_2O$$

$$l\text{-}CHPhCl\cdot CH_2\cdot CO_2H \xleftarrow{SOCl_2} l\text{-}OH\cdot CHPh\cdot CH_2\cdot CO_2H.$$

During the past year several suggestions have been put forward regarding the processes which bring about the Walden inversion. These are of especial interest, as they involve the abandonment of the idea that a carbon atom exerts its affinity by means of four directed units, and a reversion to the earlier conception of affinity as a force which acts uniformly outwards from the centre of the assumed spherically shaped atom.

Emil Fischer [41] regards the Walden inversion as brought about by processes which precede substitution, and which depend on any carbon atom being able to exert an attractive force on groups not directly united with it nor forming part of the molecule in which it occurs.

[38] E. Fischer and H. Scheibler, *Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 566; *Annalen*, 1911, **383**, 337; *A.*, i, 527.

[39] For the purpose of this investigation β-aminobutyric acid, which had previously only been known in the racemic form, was resolved into its active components by crystallisation of the *d*-camphorsulphonate of its methyl ester; the salt which first separates contains the ester of the laevorotatory amino-acid in excess.

[40] A. McKenzie and F. Barrow, *Trans.*, 1911, **99**, 1910.

[41] E. Fischer, *Annalen*, 1911, **381**, 123; *A.*, i, 418.

He considers that when an atom or group connected to a carbon atom is replaced, the replacing atom or group need not necessarily enter in the place of the one which separates, but may just as well take up another position, which will naturally lead to a different configuration when the substitution takes place on an asymmetric carbon atom. In other words, the Walden inversion is not to be regarded as a transformation in the ordinary sense, but as a normal process which in general can occur as easily as its opposite.

Whether the configuration remains the same during substitution or is changed, or whether racemisation occurs, is conditioned, on the one hand, by the nature of the substituting agent employed, and on the other hand by the nature of the groups attached to the asymmetric carbon atom.

Rejecting the conception of directed valencies, he falls back on the old idea, revived by Werner, of affinity as a force which acts from the centre of the assumed spherical atom to all parts of the surface. He regards substitution as taking place by the formation of an additive compound, which subsequently breaks down in a manner which may not or may cause a new spatial arrangement of the groups attached to the carbon atom according as the new group enters in the place previously occupied by the detached group or elsewhere.

In the latter case, if substitution takes place on an asymmetric carbon atom, change of configuration occurs. Both modes of decomposition may go on simultaneously, when racemisation, which may either be partial or complete, occurs. This well agrees with experience, for in all substitution on an asymmetric carbon atom a part of the product is always racemised, but cases in which racemisation occurs exclusively or in predominating amount he regards as abnormal.

In order to represent the views thus outlined, he uses a very ingeniously constructed model.

A small wooden sphere covered with bristles serves for the carbon atom, whilst the attached groups or atoms are represented by coloured celluloid balls fastened by a wooden peg to a piece of cork, also provided with bristles. The attached groups can thus conveniently be fixed in any position on the carbon atom and as easily removed, and if the bristle-covered faces fastened to the celluloid balls are so large that they occupy the main part of the spherical surface of the carbon atom, an arbitrary change of the spatial order is prevented.

In using the model one is at liberty to assume that all the four substituents may shift themselves at the same time and in the same sense over the spherical surface, or that the single substituents may make restricted movements into positions adjacent to the previous positions of equilibrium.

The formation of additive compounds through the so-called residual affinity or auxiliary valencies may be shown on the model by the use of the device represented in Fig. 2, made out of a wedge-shaped piece of cork furnished with brushes, and a wooden peg also terminated by a brush. The molecule to be added may be affixed to the carbon atom by the opposite brush surfaces.

As an example, Fischer illustrates by the use of this model the transformation of an active α-bromopropionic acid into a corresponding α-amino-acid through the agency of ammonia.

For the sake of simplicity he assumes that the additive compound consists of one molecule of ammonium α-bromopropionate and one molecule of ammonia. This is shown in Fig. 1. The balls numbered

Fig. I.

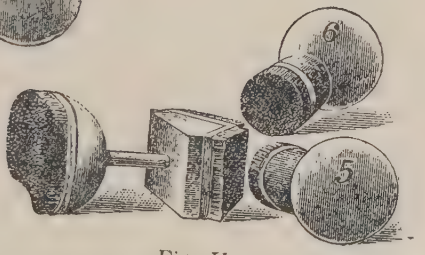


Fig. II

1, 2, 3, and 4 represent the four groups H, Br, CH_3, and CO_2NH_4 attached to the asymmetric carbon atom; the balls numbered 5 and 6 represent the NH_2 group and the hydrogen atom into which the molecule NH_3 must divide before substitution takes place. These are to be attached to the carbon atom by its residual valency, as shown in the figure, although Fischer is careful to state that this is not an essential condition of his theory, but is assumed for the sake of simplicity. If now the halogen (numbered 2) is liberated from the carbon atom, either the NH_2 group (numbered 5) can take its place, the configuration being thus not altered, or one of

the three other substituents may move into the position originally occupied by the halogen, and therefore leave its place vacant for the NH_2 to pass into. The latter procedure represents the Walden inversion.

If, finally, both processes occur simultaneously, partial or complete racemisation follows.

Werner[42] has reached very similar conclusions regarding the nature of the process causing the Walden inversion.

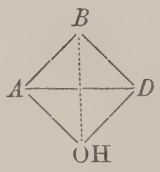
From a study of many complex inorganic compounds he has been led to conclude that the central atom of a complex radicle is able to exert an attraction on groups outside its first sphere of influence, that is, outside the space occupied by the atoms or groups directly attached to it, the magnitude of the attraction which tends to draw them into the first sphere depending on the nature of all the groups.

As the attractive force of the central atom on outside groups is concentrated in a definite direction in space, the position within the first sphere which is taken up by any entering group must correspond with this, and consequently be a definite one.

The entry of a new group into the first sphere of attraction of a saturated molecule can only occur if some other group passes out of this sphere. Naturally, that group will be expelled which is least firmly attached, and this will not in any way be determined by the position which the entering group takes up.

Therefore, when an atom or group attached to a central asymmetric carbon atom is replaced by another, the position taken up by the entering substituent is not dependent on the position of the group ultimately replaced, but is only dependent on the direction in which the carbon atom exerts its residual affinity. This is determined by the combined effect of all the groups already present and by the nature of the attracted molecule, and may consequently lead to change of configuration.

Considering, for example, the replacement by halogen of a hydroxyl group attached to an asymmetric carbon atom, we may represent the molecule by the formula $\overset{A}{\underset{B}{>}}C<\overset{D}{_{OH}}$, or by a tetrahedral model, thus:



[42] A. Werner, *Ber.*, 1911, **44**, 873; *A.*, i, 424.

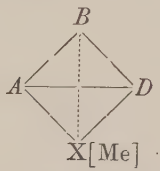
The four planes through which the attractive force of the central carbon atom may make itself felt are the planes *ABD*, *AB*(OH), *AD*(OH), and *BD*(OH).

If the attractive force of the central carbon atom happens to be exerted in the direction of one of the last three faces of the tetrahedron, the resulting new compound will correspond in configuration with the compound from which it was derived, interchange of position within the first sphere of attraction being tacitly excluded.

If the attraction, however, makes itself felt in the direction of the plane *ABD*, the optical mirror image of the former compound will be produced.

Since the residual attractive force of the carbon atom must be exerted in the direction of the same plane in the enantiomeride of the original hydroxy-compound on grounds of the general symmetry of the molecule, it follows that if the dextrorotatory halogen derivative is produced from the lævorotatory hydroxy-compound, the lævorotatory halogen derivative must be produced from the dextrorotatory hydroxy-compound.

If the halogen is again replaced by hydroxyl, for example, through the agency of a metallic hydroxide, MeOH, an intermediate additive compound, $\left[\begin{matrix} A \\ B \end{matrix} C \begin{matrix} D \\ \mathrm{XMe} \end{matrix}\right]$OH, will be formed. The direction in which the attractive force of the central carbon atom is exerted on the hydroxyl group can now be different according to the nature of the metal which has gone to the halogen atom, because the affinity which the metal has for the halogen is dependent on its nature. Considering now only the case in which under this influence the attraction of the central carbon atom is exerted outwards through one of the planes *ABX*, *ADX*, or *BDX*:



it is seen that the lævorotatory hydroxy-compound will be obtained from the lævorotatory halogen derivative and the dextrorotatory hydroxy-compound similarly from the dextrorotatory halogen derivative.

If, however, the attraction is exerted through the plane ***ABD***, each active halogen derivative will yield its hydroxyl enantiomeride.

In such a pair of operations there is a possibility of a Walden inversion being brought about in either of two ways, the change

of configuration occurring at the first or second stage. Inversion might even occur twice when the configuration of the compound ultimately obtained would be the same as that of the original one.

Werner's view differs from Fischer's, which was published simultaneously, only in attempting to give a more explicit presentment of what may actually take place during replacement.

Pfeiffer[43] has more recently stated that in consequence of his work on the molecular compounds of the tin series, he had independently developed ideas regarding the Walden inversion differing but little from those of Fischer and Werner. He agrees with them in assuming a primary addition of the reagent to the asymmetric carbon atom, but differs from Fischer in ascribing a substantial influence on the end result to the special field of the carbon atom in which addition occurs, and does not follow Werner in assuming that the primary addition takes place outside the sphere occupied by the directly attached groups. His views, however, present nothing new.

Either Fischer's or Werner's explanation of the process in which the Walden inversion is brought about, although inevitably indefinite owing to our limited knowledge of the nature of affinity, agrees well with known facts. Unfortunately we have little or no experimental evidence of the actual existence of the additive products assumed to be formed. These, however, since they only have a transient existence, must be very unstable, and it may not be possible actually to isolate them.

A further difficulty arises from the circumstance that two operations are necessary to prove the occurrence of a change of configuration. It has not hitherto been possible in the case of any pair of reactions to say with certainty in which of the two the actual change of configuration occurs, since very simple operations like the neutralisation of an acid in which no change of configuration can be regarded as probable frequently cause a reversal of the sign of rotation.

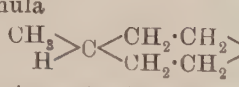
All the arguments brought forward by Walden, Fischer, and others to show that the configuration probably alters in one or other of the general reactions employed by them, appear defective when critically examined.

It may also be objected that the explanations do not allow the change of configuration likely to occur in uninvestigated cases to be predicted. We can, however, only hope to formulate definite rules after our knowledge of these transformations has been very much increased.

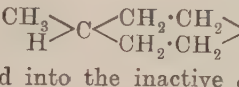
[43] P. Pfeiffer, *Annalen*, 1911, **383**, 123; *A.*, i, 788.

Molecular Asymmetry.

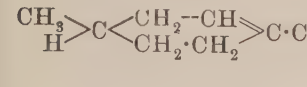
W. H. Perkin and W. J. Pope[44] have published a paper on the "Optically Active Derivatives of 1-Methyl*cyclo*hexylidene-4-acetic Acid." The paper also contains an account of some optically inactive compounds derived from the same acid. The acid itself, having the formula



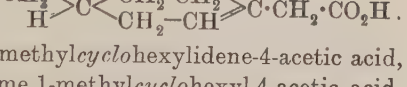
was resolved into its optically active components *d*- and *l*- by Perkin, Pope, and Wallach.[45] The same authors also found that the inactive *dl*-acid could be converted into the inactive *dl*-1-methyl-Δ^3-*cyclo*hexene-4-acetic acid by the shifting of the double linking from the $\alpha\beta$- to the $\beta\gamma$-position. The latter acid was discovered originally by Marckwald and Meth.[46] Perkin and Pope now find that the active *l*-1-methyl*cyclo*hexylidene-4-acetic acid is also converted into the inactive *dl*-acid of Marckwald and Meth. The optically active acid:



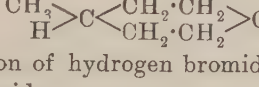
is here converted into the inactive *dl*-mixture:



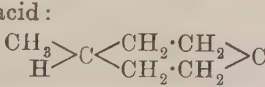
and



The addition of hydrogen to 1-methyl*cyclo*hexylidene-4-acetic acid, whether *dl*-, *d*-, or *l*-, gave the same 1-methyl*cyclo*hexyl-4-acetic acid, of the formula:

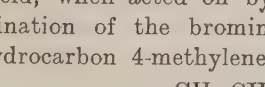


and the addition of hydrogen bromide gave 4-bromo-1-methyl*cyclo*hexyl-4-acetic acid:



Both the hydrogenated and the bromo-saturated acids were optically inactive. This is in accordance with the theory, the two formulæ only admitting of a *cis*- and *trans*-isomerism respectively without rotatory power.

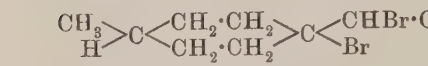
The bromo-acid, when acted on by sodium carbonate solution, gave, by elimination of the bromine and carboxyl groups, the unsaturated hydrocarbon 4-methylene-1-methyl*cyclo*hexane,



[44] *Trans.*, 1911, **99**, 1510. [45] *Ibid.*, 1909, **95**, 1785.
[46] *Ber.*, 1906, **39**, 1171, 2404; *A.*, 1906, i, 360, 663.

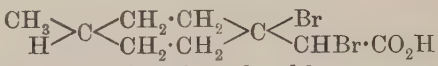
This hydrocarbon is the same as that obtained by Wallach[47] by the slow distillation, both of the original unsaturated acid, and also of Marckwald and Meth's acid. This hydrocarbon is also inactive, its formula not admitting either of optical or of *cis*- and *trans*-isomerism.

The addition of bromine to the unsaturated acid furnishes compounds of especial interest. Here, in addition to a *cis*- and *trans*-isomerism, there is also asymmetry of the molecule giving rise to the possibility of four isomerides. These four isomerides have been obtained by the authors. Their constitution is represented by the following formulæ:



Cis-form, *d*- and *l*-.

and



Trans-form, *d*- and *l*-.

The authors having at present no method for discriminating between the *cis*- and *trans*-forms, propose to distinguish the two forms provisionally as α- and β-isomerides. The four isomerides showed the following properties:

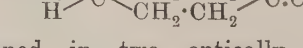
l-β-acid, m. p. 154°, $[\alpha]_D$ −24·5°.
d-β-acid, m. p. 154°, $[\alpha]_D$ +24·3°.
l'-α-acid,[48] m. p. 102°, $[\alpha]_D$ +8·6°.
d'-α-acid,[48] m. p. 102°, $[\alpha]_D$ not determined.

The properties of the racemic mixtures were:

dl-β-acid, m. p. 145—146°, inactive.
d'l'-α-acid, m. p. 105—106°, inactive.

The *l*-1-methyl*cyclo*hexylidene-4-acetic acid gives the *l'*-α- and the *l*-β-dibromides, whilst the *d*-unsaturated acid gives the other two isomerides. The sign of rotation is unchanged for the β-acids, and reversed for the α-acids.

When the dibromide is acted on by sodium carbonate solution, the carboxyl group is eliminated with bromine in the β-position, and 1-methyl-4-bromomethylene*cyclo*hexane is obtained:



This was obtained in two optically opposite forms, *d'*- of $[\alpha]_D$ −50·39° and *l'*- of $[\alpha]_D$ +50·18°. The α- and β-forms of the

[47] *Annalen*, 1906, **347**, 345; 1909, **365**, 267; *A.*, 1906, i, 563; 1909, i, 383.

[48] To avoid any possible confusion the suggestion of E. Fischer (*Ber.*, 1907, **40**, [i], 102) as to nomenclature has been adopted; thus *l* represents a lævorotatory compound obtained from a lævo, whilst *l'* represents a dextrorotatory compound obtained from a lævo. *d* and *d'* are used in a similar sense.

dibromide gave the same product. The sign of rotation is reversed from that of the parent unsaturated acid.

By the addition of chlorine to the compound just described, a dichloride was obtained of the formula:

$$\begin{matrix}CH_3\\H\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!\!>\!CCl\cdot CHBrCl.$$

This compound was optically active, but had a very slight rotatory power, the *d*-form giving $[\alpha]_D + 0{\cdot}35°$, with another reversal of sign from that of the last-mentioned compound. The authors suggest that the low rotatory power may be due to the preparation being a mixture of dextro- and lævo-α- and β-isomerides. The action of concentrated potassium hydroxide solution on the dibromide of the original acid gave a bromo-unsaturated acid of the formula:

$$\begin{matrix}CH_3\\H\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!\!>\!C\!:\!C\!<\!\!\begin{matrix}CO_2H\\Br\end{matrix}.$$

Here, also, the α- and β-isomerides gave the same unsaturated acid, and there is no reversal of sign from that of the original substance: *d*-acid, $[\alpha]_{Hg\ green} + 12{\cdot}8°$; *l*-acid, $[\alpha]_{Hg\ green} - 12{\cdot}4°$.

Perkin, Pope, and Wallach[49] claimed that in 1-methyl*cyclo*hexylidene-4-acetic acid there is no asymmetric atom. This view has been criticised by Everest,[50] who considers that carbon atom (1) is asymmetric:

$$\begin{matrix}CH_3\\H\end{matrix}\!\!>\!\underset{(1)}{C}\!<\!\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!\!>\!\underset{(4)\ (7)}{C\!:\!C}\!<\!\!\begin{matrix}H\\CO_2H\end{matrix},$$

because the configuration of the molecule is not the same when taken either way round the ring relative to the carbon atom (1).

Perkin and Pope reply that their original conclusion stands, and add: "If Everest's view that a carbon atom is non-asymmetric only when 'the configuration of the remainder of the molecule is the same when taken either way, relative to the carbon atom,' is accepted, every atom, carbon, oxygen, or hydrogen, in the molecule of 1-methyl*cyclo*hexylidene-4-acetic acid—and, indeed, of any optically active substance—is asymmetric."

It does not seem clearly indicated here what the authors would have us to understand by asymmetric hydrogen and oxygen atoms; as regards carbon, however, their contention cannot be sustained, inasmuch as the greater number of the carbon atoms, being attached by two at least of their affinities to the same groups, for example, hydrogen atoms, must, *ex hypothesi*, be symmetrical, whatever may be the nature of the other groups to which they are attached.

Everest has replied,[51] upholding his view. Marsh[52] asserts that

[49] *Loc. cit.* [50] *Chem. News*, 1909, **100**, 295; *Proc.*, 1911, **27**, 285.
[51] *Proc.*, 1911, **27**, 285. [52] *Ibid.*, 317.

the three carbon atoms (1), (4), and (7) are asymmetric, in accordance with the definition given by him in 1888.[53]

It may here be recalled that van't Hoff in 1874 defined an asymmetric carbon atom to be an atom combined with four different groups. In 1887 he explained why he called it asymmetric. It was not called asymmetric because it was combined with four different groups, but "il a été appelé asymétrique parceque toute symétrie fait défaut dans le groupement qu'il relie.[54]

Every optically active compound must contain an asymmetric atom, although it did not follow that the presence of asymmetric carbon in a molecule necessarily entailed optical activity. Van't Hoff, in 1874, had explained isomerism of the maleic and fumaric types, and in *La Chimie dans l'espace* (1875) extended his views to ring-linking isomerism and to the type $\overset{a}{\underset{b}{>}}C{:}C{:}C<\overset{d}{\underset{e}{}}$, where he predicted optical activity.

In 1888 Baeyer[55] discovered the isomeric hexahydroterephthalic acids, and explained their isomerism on the analogy of maleic and fumaric acids, introducing the terms *cis-cis* for the maleinoid and *cis-trans* for the fumaroid forms. He considered the carbon atoms to which the carboxyl groups are attached to be asymmetric, both when linked in the ring and also when doubly linked, and for this kind of asymmetry where there is no optical activity, and where the asymmetry of each atom depends on that of both, he proposed the term "relative asymmetry." In 1888 Marsh,[56] holding the view that a carbon atom situated in a ring could not be regarded in any real sense as combined with four different groups, suggested as a test of asymmetry that, if any two groups attached to one of the carbon atoms by exchanging positions bring about a change in the formula as a whole, that carbon atom will be asymmetric. This exchange of groups he called the replacement of the carbon atom by its image. The formula obtained by this replacement may be the mirror image of the original one, or may differ from it in other respects without being necessarily itself asymmetric.

With regard to the particular instance under consideration here (1-methyl*cyclo*hexylidene-4-acetic acid), it is clear that the exchange of position of methyl and hydrogen attached to C(1) changes the whole formula into its mirror image. The same change is brought about if the ring attachments to C(4) are reversed, and also by exchanging the positions of the CO_2H and H attached to C(7). On the other hand, no change is brought about in the formula if the groups attached to any one of the other carbon atoms change places.

[53] *Phil. Mag.*, 1888, [v], **26**, 426.

[54] *Dix années dans l'histoire d'une théorie*, 1887, p. 25.

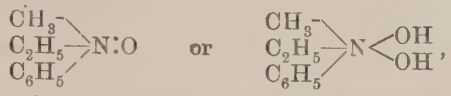
[55] *Annalen*, 1888, **245**, 128 ; *A.*, 1888, 1069.

[56] *Loc. cit.*

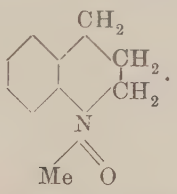
Optically Active Amino-oxides.

Although according to current views compounds of the type Na_2bcd should exist in two enantiomerides, up to a few years ago the actual isolation of such active compounds had not been realised. Meisenheimer [57] then showed that methylethylaniline oxide, which is a weak base, could be resolved into two active components by conversion into its *d*-camphorsulphonate.

At that time it could not be decided whether the free active bases ought to be regarded as true amino-oxides or as the corresponding dihydroxy-compounds:



as they could only be obtained as viscid, hygroscopic liquids. The question has now been decided in favour of the first alternative, both the dextrorotatory and the lævorotatory enantiomeride having been obtained [58] in crystalline form, and their rotations measured when dissolved in anhydrous benzene. In this solvent the compounds can only be present as oxides, although it is possible that in aqueous solution they exist in the dihydroxylic forms. Methylethyl-β-naphthylamine oxide has also been prepared and similarly resolved, as has also kairoline oxide, a cyclic amino-oxide:



It is therefore probable that all amino-oxides and other compounds containing nitrogen, doubly linked to oxygen and also attached to three different groups, can exist in two enantiomeric forms. Up to the present all attempts to resolve compounds with a double linking between the central nitrogen atom and carbon have failed, and it seems probable that such compounds can only exist in one inactive form.

These consequences follow from the assumption that the four non-ionisable radicles group themselves about the central nitrogen atom in a first sphere of attraction in the relative positions of the angles of a tetrahedron, of which it is the centre, whilst the ionisable mobile group is more loosely attached in a second outer zone in some position opposite the centre of one of the tetrahedral faces.

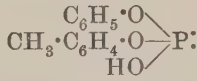
[57] J. Meisenheimer, *Ber.*, 1908, **41**, 3966; *A.*, 1909, i, 20.
[58] J. Meisenheimer, *Annalen*, 1911, **385**, 117; *A.*, 1912, i, 25.

Meisenheimer considers that the different behaviour of compounds containing nitrogen doubly linked to carbon or oxygen may be explained on the assumption that in the former class the double linking takes the place of two non-ionisable radicles of the group N*abcde*, whilst in the latter it replaces the ionisable and one of the non-ionisable groups. It is seen that only in the latter case are enantiomerides possible.

Optically Active Phosphorus Compounds.

Two years ago some indications that certain derivatives of phosphorus should be capable of resolution into optically active constituents were observed.[59]

The behaviour of the *l*-menthylamide of phenyl *p*-tolyl hydrogen phosphate:

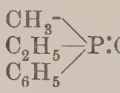


pointed to its being a mixture.

By fractional crystallisation this amide was separated into two isomerides. For the more sparingly soluble or α-isomeride, which melted at 110°, $[\alpha]_D = -32{\cdot}3°$, whilst for the β-isomeride obtained from the mother liquor of the α-form, and probably not quite free from it and which melted at 85—86°, $[\alpha]_D = -37{\cdot}9°$.

The *l*-menthylamide of phenyl β-naphthyl hydrogen phosphate can be similarly separated[60] into a sparingly soluble and a more soluble constituent. The first or α-isomeride melts at 135—136°, and gives $[\alpha]_D$ −37·2°; the second or β-isomeride melts at 94—96°, and gives $[\alpha]_D$ about −29°.

Meisenheimer and Lichtenstadt[61] have recently shown that phenylmethylethylphosphoric oxide:



can exist in optically active forms, and have thus first obtained a derivative of phosphorus, the optical activity of which is without doubt due to the asymmetric distribution of the radicles around the phosphorus atom.

They were led to attempt the resolution of this compound by the surprising ease with which the racemic amino-oxides could be separated into pure optically active components; this was effected

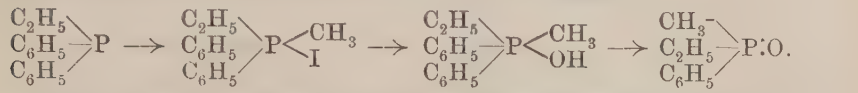
[59] B. D. W. Luff and F. S. Kipping, *Trans.*, 1909, **95**, 1993.

[60] F. S. Kipping and F. Challenger, *ibid.*, 1911, **99**, 626.

[61] J. Meisenheimer and L. Lichtenstadt, *Ber.*, 1911, **44**, 356; *A.*, i, 344.

in the case, for example, of kairoline oxide by a single crystallisation of the *d*-tartrate or *d*-bromocamphorsulphonate.

The phenylmethylethylphosphoric oxide required was prepared by combining methyl iodide with diphenylethylphosphine, and then heating the base set free from this by silver oxide with water, when benzene was split off and the oxide obtained:



When brought together with the equivalent quantity of *d*-bromocamphorsulphonic acid dissolved in ethyl acetate, the base and acid combine, and after a time a well crystallised salt separates.

This melts at 94—95°, and in aqueous solution gives $[\alpha]_D$ +67·4°, these values not changing on recrystallisation.

The value $[M]_D$ +323° for the rotation, obtained from this, indicates the presence of an optically active phosphorus ion, PhMeEtP·OH, with a rotation of +48°.

This optical activity can only arise from the asymmetric grouping of the radicles about the phosphorus atom, which, therefore, like the nitrogen atom, can give rise to optically active compounds when its five valencies are saturated by different radicles.

The phenylmethylethylphosphoric oxide which is obtained as a colourless, crystalline compound by passing dry ammonia into a benzene solution of the *d*-bromocamphorsulphonate of the active base is also optically active, having $[\alpha]_D$ +23·1° in water, +25° in *N*-hydrochloric acid, and +33·8° in benzene.

This shows that, as with nitrogen, the saturation of the five valencies of a phosphorus atom by only four different radicles is sufficient to give an asymmetric configuration to the molecule.

Asymmetric Cobalt Compounds.

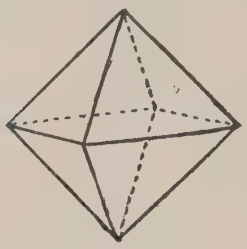
Werner's theory of molecular compounds based on the assumption of principal and auxiliary valencies has been frequently applied by him with great success to group together numerous classes of compounds not previously very clearly brought into relation.

During the past year a number of deductions from this theory relating to the possibility in certain cases of the existence of enantiomerides have been most strikingly verified, and have given a weighty confirmation of the fundamental correctness of the underlying assumptions.

According to this theory the six groups, so frequently associated with a metallic atom in complexes[62] of the form [Me A_6], are

[62] Me = metallic atom. A or B = co-ordinated atom or group.

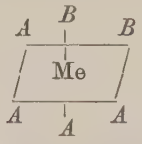
arranged in space around this central atom in the relative positions of the angles of an octahedron (I), which is conventionally represented and numbered as in (II):



(I.)

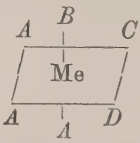
(II.)

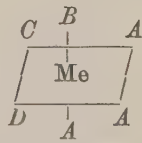
This representation leads to various conclusions capable of being put to the test of experiment; for example, when the six co-ordinated groups are the same, as in [Me A_6], or contain a single other group as in $\left[\mathrm{Me}\begin{matrix}A_5\\B\end{matrix}\right]$, the resulting compounds should exist in one form only, whilst those having the composition $\left[\mathrm{Me}\begin{matrix}A_4\\B_2\end{matrix}\right]$ should exist in *cis*- and *trans*-isomeric series, having configurations which may be represented thus:



This important deduction, as is well known, has been confirmed in the case of compounds of the elements platinum, cobalt, and chromium.

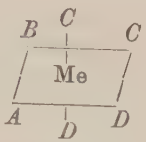
Again, in certain cases the theory predicts the existence of optical isomerism; for example, if the groups *B*, *C*, and *D* are situated relatively to the central atom in the positions of the angles of one face of the octahedron, compounds containing complex radicles of the form $\left[\begin{matrix}B\\C\end{matrix}\mathrm{Me}\begin{matrix}A_3\\D\end{matrix}\right]$ should give pairs of optically opposed isomerides of the configurations:





whilst compounds containing complexes of the composition $\left[\begin{matrix}A\\B\end{matrix}\mathrm{Me}\begin{matrix}C_2\\D_2\end{matrix}\right]$, if the groups attached to the metallic atom have the

following relative positions, should similarly be capable of resolution into oppositely active components:



In such compounds it is not indeed necessary for four or even three different groups to be present if two pairs are connected, for only a different spacial orientation of the connecting chain is needed to cause molecular asymmetry.

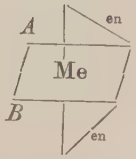
Such a possibility exists, for example, in compounds where the groups *C C* and *D D* are replaced by ethylenediamine,

$$(NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2 = en),$$

that is, among compounds containing the complex radicles:

$$\left[\begin{matrix} A \\ B \end{matrix} Me\, en_2\right] \quad \text{or} \quad \left[\begin{matrix} A \\ A \end{matrix} Me\, en_2\right] \quad \text{or} \quad [Me\, en_3].$$

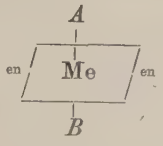
If the configuration formulæ of such compounds are constructed for the cases where the groups *A B* and *A A* are attached to adjacent angles, that is, are in the *cis*-position, it is seen that in both non-superposable mirror images are possible:



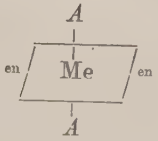
(I.)

(II.)

whilst in the cases in which the *A* and *B* or *A* groups are in the *trans*-position the mirror images are superposable:



(III.)



(IV.)

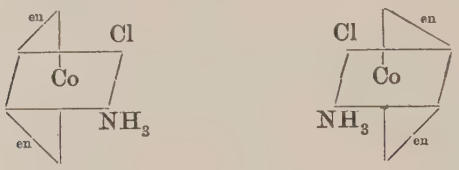
Compounds of the types (I) and (II) should therefore be capable of resolution into optically opposed active components, whilst compounds of the types (III) and (IV) should not be so resolvable.

Numerous examples of these types are known among the compounds of cobalt, and Werner has recently been able to resolve members of the first two classes into their optical enantiomerides, and to show that members of the last two cannot be so resolved.

Among compounds of the first type members of the following two series:

$$\left[\begin{matrix}\mathrm{Cl}\\ \mathrm{H_3N}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{X_2}$$

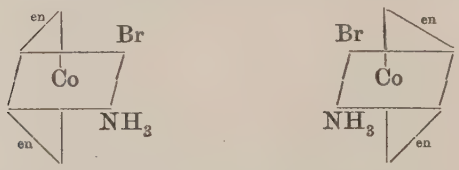
1-Chloro-2-amminediethylenediaminecobaltic salts.



and

$$\left[\begin{matrix}\mathrm{Br}\\ \mathrm{H_3N}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{X_2}$$

1-Bromo-2-amminediethylenediaminecobaltic salts.



by the help of the *d*-bromocamphorsulphonates have been resolved [63] into optically active components, which may be represented by the above configuration formulæ. In both cases the *d*-bromocamphorsulphonate of the *d*-form is less soluble than that of the *l*-form.

The procedure adopted was as follows: 1-chloro-2-amminediethylenediaminecobaltic chloride, $\left[\begin{matrix}(1)\ \mathrm{Cl}\\ (2)\ \mathrm{H_3N}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{Cl_2}$, dissolved in warm water was mixed with a solution of the silver salt of *d*-bromocamphorsulphonic acid of appropriate strength. After separation of the silver chloride, the *d*-chloroamminediethylenediaminecobaltic *d*-bromocamphorsulphonate first crystallised out, the mother liquor from these crystals then solidifying after some hours to a pulp of crystals of the corresponding lævo-salt. Each could be recrystallised from hot water. The corresponding active bromo-salts were similarly obtained.

[63] A. Werner, *Ber.*, 1911, **44**, 1887; *A.*, i, 613.

From the *d*-bromocamphorsulphonates other salts can be prepared without difficulty. The bromides, for example, are obtained by adding concentrated hydrobromic acid to the sulphonates. The latter dissolve, and after a short time the bromides crystallise out.

The rotatory power of the salts of the active components is considerable. For the 1-chloro-2-amminediethylenediaminecobaltic bromides, $[\alpha]_c = \pm 43°$; for the 1-bromo-2-amminediethylenediaminecobaltic bromides, $[\alpha]_c = \pm 46{\cdot}25°$.

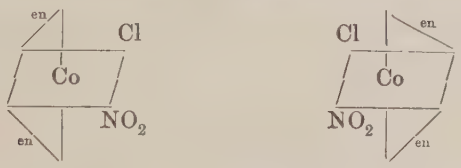
The active compounds are very stable; the aqueous solutions of the bromides, for example, $\left[\begin{matrix}\mathrm{Br}\\ \mathrm{H_3N}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{Br_2}$, can be kept for a long time at the ordinary temperature or even heated just to boiling without undergoing racemisation.

The activity is also maintained when the non-ionisable halogen atom in the complex radicle is removed with silver nitrate according to the equation:

$$\left[\begin{matrix}\mathrm{Br}\\ \mathrm{H_3N}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{Br_2} + 3\mathrm{AgNO_3} + \mathrm{H_2O} = \left[\begin{matrix}\mathrm{H_2O}\\ \mathrm{H_3N}\end{matrix}\mathrm{Co\,en_2}\right](\mathrm{NO_3})_3 + 3\mathrm{AgBr},$$

showing that the aquoamminediethylenediaminecobaltic salts also can exist in optically active forms.

A further increase[64] in our knowledge of this type of compound has resulted from the resolution of 1-chloro-2-nitrodiethylenediaminecobaltic salts of the general formula $\left[\begin{matrix}\mathrm{Cl}\\ \mathrm{O_2N}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{X}$ into optically active components, which may be represented:



These differ from the 1-halogen-2-amminediethylenediaminecobaltic salts in the circumstance that they contain two acid residues within the complex $\left[\begin{matrix}\mathrm{Cl}\\ \mathrm{O_2N}\end{matrix}\mathrm{Co\,en_2}\right]$, which in consequence is univalent, whilst in salts of the former class only one acid residue is included within the bivalent complex $\left[\begin{matrix}\mathrm{X}\\ \mathrm{H_3N}\end{matrix}\mathrm{Co\,en_2}\right]$.

Resolution was effected by taking advantage of the circumstance that *l*-1-chloro-2-nitrodiethylenediaminecobaltic *d*-camphorsulphonate is sparingly soluble, and *d*-1-chloro-2-nitrodiethylenediaminecobaltic *d*-camphorsulphonate is very easily soluble, whilst the

[64] A. Werner, *Ber.*, 1911, **44**, 3272; *A.*, 1912, i, 10.

reverse is the case with the corresponding *d*-bromocamphorsulphonates.

The difference in solubility is so great that on mixing a concentrated solution of racemic 1-chloro-2-nitrodiethylenediaminecobaltic chloride with a suitably concentrated solution of ammonium *d*-camphorsulphonate or *d*-bromocamphorsulphonate respectively, the corresponding salt of the lævo- or dextro-component separates in a pure condition. The active 1-chloro-2-nitrodiethylenediaminecobaltic salts show the phenomenon of mutarotation in aqueous solution, the initial rotation not remaining constant, but rapidly increasing; $[\alpha]_D$ initially $= 20°$, rapidly increases to 52°, where it remains constant. This is due to the conversion of the chloronitro- into the aquonitro-salt, the non-ionisable chlorine atom showing a relatively great reactivity, and in aqueous solution going with readiness into ionisable union, thus:

$$\left[\begin{matrix}\mathrm{Cl}\\ \mathrm{O_2N}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{Cl} + \mathrm{H_2O} = \left[\begin{matrix}\mathrm{H_2O}\\ \mathrm{O_2N}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{Cl_2}.$$

The aquonitro-salts, like the aquoammine salts, can therefore exist in optically active forms.

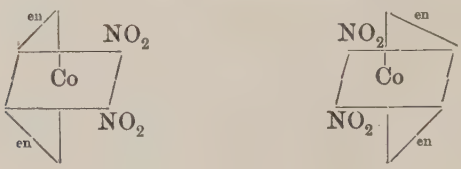
The active chloronitro-salts can be converted into other series of similar compounds without loss of optical activity, for example, by the action of potassium thiocyanate the active thiocyanatonitro-compounds are produced, thus:

$$\left[\begin{matrix}(1)\ \mathrm{Cl}\\ (2)\ \mathrm{O_2N}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{Cl} + 2\mathrm{KNCS} = 2\mathrm{KCl} + \left[\begin{matrix}\mathrm{SCN}\\ \mathrm{O_2N}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{NCS}.$$

Among compounds of the second type members of the following two series have been resolved into active compounds, the configuration of which is shown:

$$\left[\begin{matrix}(1)\ \mathrm{O_2N}\\ (2)\ \mathrm{O_2N}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{X}$$

1 : 2-Dinitrodiethylenediaminecobaltic salts.[65]

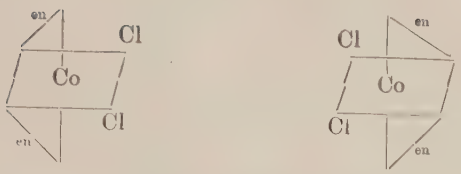


and

$$\left[\begin{matrix}(1)\ \mathrm{Cl}\\ (2)\ \mathrm{Cl}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{X}$$

1 : 2-Dichlorodiethylenediaminecobaltic salts.[66]

[65] A. Werner, *Ber.*, 1911, **44**, 2445; *A.*, i, 838.
[66] A. Werner, *ibid.*, 3279; *A.*, 1912, i, 10.



In each series resolution was effected by a method resembling that used with the analogous chloronitro-salts. It consists in throwing out of solution the more sparingly soluble camphorsulphonate or bromocamphorsulphonate by the help of the ammonium salts of the two acids, the relative solubility of the salts of the active radicles being found in all cases to be reversed in the case of the two acids, that is, if the *d*-camphorsulphonate of the lævo-base is the less soluble, the *d*-bromocamphorsulphonate of the dextro-base is the less soluble, and vice versa; for example, *l*-dinitrodiethylenediaminecobaltic *d*-camphorsulphonate is sparingly soluble, whilst the corresponding salt of the *d*-radicle is easily soluble; on the other hand, when *d*-bromocamphorsulphonic acid is used, the less soluble salt is that yielded by the *d*-radicle. The *d*-camphorsulphonate of the *l*-radicle and the *d*-bromocamphorsulphonate of the *d*-radicle can thus be obtained pure, and serve for the preparation of their salts.

The observed specific rotations of the 1:2-dinitrodiethylenediaminecobaltic salts are of the same order as those observed with the active chloro- and bromo-amminediethylenediaminecobaltic salts; for example, in 1 per cent. solutions the following were obtained [67]: chloride, $[\alpha]_D \, {}^{+40^\circ}_{-50^\circ}$; bromide, $[\alpha]_D \, {}^{+42{\cdot}5^\circ}_{-44^\circ}$.

The active 1:2-dinitrodiethylenediaminecobaltic salts show a very pronounced anomalous rotation dispersion, the *D* line being strongly rotated, whereas the *C* line is rotated to a very small extent or not at all.

The rotatory power of the active dichlorodiethylenediaminecobaltic salts is very much greater than that of salts of the other optically active cobalt series; for example, for the chloride, $[Cl_2Co\,en_2]Cl$, $[\alpha] \, {}^{-200^\circ}_{+184^\circ}$.

Whilst the chloroammine-, bromoammine-, and dinitro-cobaltic salts are stable in aqueous solution and show a constant rotatory power, the rotatory power of the dichlorocobaltic salt diminishes very rapidly, and as a rule after some hours completely disappears. This is due to the action of the water used as solvent, for in the dry state their activity remains unchanged. The auto-racemisation of these salts is connected with the fact that the dichloro-salts take

[67] A. Werner, *Ber.*, 1911, **44**, 2445; *A.*, i, 838.

up water, being converted into the chloroaquo- and diaquo-salts, thus:

$$[Cl_2Co\,en_2]Cl + H_2O = \begin{pmatrix} H_2O \\ Cl \end{pmatrix} Co\,en_2 \Big) Cl_2,$$

and

$$\begin{bmatrix} H_2O \\ Cl \end{bmatrix} Co\,en_2 \Big] Cl_2 + H_2O = \begin{bmatrix} H_2O \\ H_2O \end{bmatrix} Co\,en_2 \Big] Cl_3.$$

Whether it is a consequence of the formation of a *trans*-compound or of some other kind of change has not yet been decided.

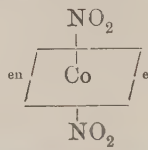
In certain cases the two intra-radicle chlorine atoms of the dichloro-salts can both be replaced by other acid residues without loss of optical activity. This is brought about, for example, by the action of potassium carbonate, which causes the formation of a carbonatodiethylenediaminecobaltic salt. By this replacement, which can be formulated thus:

$$[Cl_2Co\,en_2]Cl + K_2CO_3 \longrightarrow \left[OC\!<\!\begin{matrix} O \\ O \end{matrix}\!>\!Co\,en_2\right]X,$$

there is formed an active carbonato-salt which is relatively easy to isolate. The direction of rotation of the carbonato-salt formed is opposite to that of the dichloro-salt from which it is produced.

The experimental evidence given so far has been of a positive character. The theory, however, also requires that compounds of the composition $[A_2Me\,en_2]X$, in which the A radicles are in the *trans*-position, should not exist in optically active form.

In agreement with this prediction Werner has shown [68] that it is not possible to separate the 1 : 6-dinitrodiethylenediaminecobaltic salts which have the nitro-groups in the *trans*-position, thus:



into active components, although a splendidly crystallised camphor-sulphonate of this radicle can be obtained.

Werner [69] notes that the mirror image isomerism of compounds of the second type is of a simpler nature than that of the first, inasmuch as a less number of distinct groups are involved.

He considers that compounds of type I contain an asymmetric cobalt atom, whilst compounds of type II possess a kind of molecular asymmetry, which he designates as molecular asymmetry I, since the octahedral formula admits of still other kinds of molecular asymmetry. The distinction, however, can scarcely be

[68] A. Werner, *Ber.*, 1911, **44**, 2454 ; *A.*, i, 839.
[69] A. Werner, *ibid.*, 2446 ; *A.*, i, 839.

justified. What is established in both cases is the fact that a metallic atom can act as the central atom of a stable asymmetrically ordered molecule, in which there exists no plane of symmetry, and it might perhaps be well to abandon the current mode of speaking of an asymmetric atom, reserving the term asymmetric for the entire molecule, to which alone it can be consistently applied.

The results above outlined show that Werner's conception of the octahedral structure of these compounds is capable of withstanding the severest tests to which a theory can be subjected, since it continually leads to predictions which subsequent experiments most strikingly verify.

They also appear to negative the idea that there is any real difference between ordinary compounds and the so-called molecular compounds.

The cases of isomerism known up to the present time among the diacidodiethylenediaminecobaltic salts are summarised by Werner [70] as follows:

(1) *Cis-trans*-isomerism:

$$\left[\begin{matrix}(1)\ O_2N \\ (2)\ O_2N\end{matrix}\text{Co en}_2\right]X \quad \text{and} \quad \left[\begin{matrix}(1)\ O_2N \\ (6)\ O_2N\end{matrix}\text{Co en}_2\right]X$$

Flavo-salts. Croceo-salts.

(2) Salt-isomerism:

$$\left[\begin{matrix}(1)\ ON\cdot O \\ (2)\ ON\cdot O\end{matrix}\text{Co en}_2\right]X \quad \text{and} \quad \left[\begin{matrix}(1)\ O_2N \\ (2)\ O_2N\end{matrix}\text{Co en}_2\right]X$$

1 : 2-Dinitritodiethylenediaminecobalti-salts. Flavo-salts.

and also the 1 : 6-dinitrodiethylenediaminecobaltic salts and the croceo-salts.

(3) Ionisation metamerism:

$$\left[\begin{matrix}O_2N \\ O_2N\end{matrix}\text{Co en}_2\right]X \quad \text{and} \quad \left[\begin{matrix}O_2N \\ X\end{matrix}\text{Co en}_2\right]NO_2.$$

X can be either Cl, Br, or SCN, etc.

(4) Co-ordination polymerism:

$$\left[\begin{matrix}O_2N \\ O_2N\end{matrix}\text{Co en}_2\right]_3\left[\text{Co}(NO_2)_6\right] \quad \text{and} \quad \left[\text{Co en}_3\right]\left[\text{Co}(NO_2)_6\right].$$

(5) Mirror image isomerism:

$$d\text{- and } l\text{-}\left[\begin{matrix}(1)\ O_2N \\ (2)\ O_2N\end{matrix}\text{Co en}_2\right]X.$$

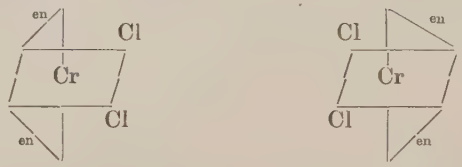
Asymmetric Chromium Compounds.

As the co-ordinated compounds of chromium show great analogy with those of cobalt, the discovery of optically active cobalt deriv-

[70] *Ber.*, 1911, **44**, 2449 ; *A.*, i, 840.

atives led to the conclusion that the corresponding chromium compounds, if obtainable, should be similarly capable of resolution into optically active components. Although up to the present no great number of chromium compounds have been prepared which should theoretically exhibit optical isomerism, Werner[71] has succeeded in resolving the members of one series, the 1 : 2-dichlorodiethylenediaminechromic salts of the composition $[Cl_2Cr\,en_2]X$, into their optically active components.

The complex radicles of the two enantiomerides are represented by the configuration formulæ:



and shows molecular asymmetry I, similar to that observed in the case of the 1 : 2-dinitro- and 1 : 2-dichloro-diethylenediaminecobaltic salts.

Like the corresponding cobaltic salts, the 1 : 2-dichlorodiethylenediaminechromic salts are very unstable in aqueous solution, as they very readily take up water and pass over into the chloroaquo- and diaquo-salts, thus:

$$\left[\begin{matrix}Cl\\Cl\end{matrix}Cr\,en_2\right]Cl + H_2O = \left[\begin{matrix}H_2O\\Cl\end{matrix}Cr\,en_2\right]Cl_2,$$

$$\left[\begin{matrix}H_2O\\Cl\end{matrix}Cr\,en_2\right]Cl_2 + H_2O = \left[\begin{matrix}H_2O\\H_2O\end{matrix}Cr\,en_2\right]Cl_3.$$

Owing to this circumstance, resolution with silver *d*-bromocamphorsulphonate could not be effected.

A method resembling that used in the case of the analogously reactive cobaltic salts was, however, successful.

It was found that when ammonium *d*-bromocamphorsulphonate was added to a freshly prepared saturated solution of racemic 1 : 2-dichlorodiethylenediaminechromic chloride, perfectly pure crystals of the *d*-bromocamphorsulphonate of the lævo-radicle quickly separated, whilst when ammonium *l*-bromocamphorsulphonate was employed, *d*-dichlorodiethylenediaminechromic *l*-bromocamphorsulphonate was similarly thrown down. From these sulphonates the chlorides, bromides, and nitrates of the two active radicles were prepared.

For the optical rotation the following values were obtained: chloride, $[\alpha]^{-140°}_{+140°}$; bromide, $[\alpha]^{-130°}_{+124°}$; nitrate, $[\alpha]^{-120°}_{+122°}$. The active dichlorodiethylenediaminechromic salts very quickly lose their

[71] A. Werner, *Ber.*, 1911, **44**, 3231; *A.* i, 951.

activity in aqueous solution; but the cause of this has not yet been fully cleared up.

The active chromic salts show a much smaller rotatory power than the corresponding cobaltic compounds, the difference in molecular rotation being about 140—150°, from which it follows that the rotatory power is dependent, not only on the nature of the groups attached to the central atom, but on that of the central atom itself.

Novel Reactions and Others of General Interest.

Among the chief reactions to be noticed under this heading are some new processes for preparing halogen derivatives. The simplest of these consists of treating the corresponding alcohol with two molecular proportions of thionyl chloride or bromide and one such proportion of a tertiary base.[72] Under favourable conditions the method gives yields of over 90 per cent., and it may be applied to alcohols of various types, for example, *iso*amyl alcohol, cinnamyl alcohol, and esters of hydroxy-acids. An advantage of the method is seen in the case of ethyl *l*-malate, where less racemisation takes place than with the use of phosphorus pentachloride. However, the process cannot be applied to phenols, and, with substances such as *cyclo*hexanol, dehydration may occur.

Another method[73] leads to these halogen derivatives from the primary amines. The benzoyl derivatives of the latter substances are warmed with phosphorus pentachloride, when the following interaction occurs:

$$R{\cdot}NH{\cdot}COPh + PCl_5 = POCl_3 + PhCN + RCl;$$

but this is by no means quantitative, and there is sometimes trouble in separating the chloride from the benzonitrile which is always formed. It is recommended that the latter be converted into the crystalline hydrochloride of benziminoethyl ether, which is very sparingly soluble in alcohol. The process has been applied to mono- and di-amines, the latter substances leading to di-halogen derivatives, such as $\alpha\mu$-dichlorododecane, which may prove of use in other synthetical reactions. The catalytic bromination of the side-chain in aromatic compounds may be effected[74] with the aid of ozone, but it remains for future research to decide whether this agent can be universally applied. An elegant method of chlorinating aromatic substances has been developed from the results of previous experiments[75] on the behaviour of *N*-chloroacylamines in

[72] G. Darzens, *Compt. rend.*, 1911, **152**, 1314, 1601; *A.*, i, 513, 517.
[73] J. von Braun and W. Sobecki, *Ber.*, 1911, **44**, 1464; *A.*, i, 597.
[74] L. Bruner and Z. Lahociński, *Bull. Acad. Sci. Cracow*, 1910, 560; *A.*, ii, 242.
[75] K. J. P. Orton and W. J. Jones, *Trans.*, 1909, **95**, 1456.

presence of hydrogen chloride. It may be recalled from former reports that when these substances are mixed under suitable conditions the reversible change (i):

$$Ar{\cdot}NCl{\cdot}Ac + HCl \rightleftarrows Ar{\cdot}NH{\cdot}Ac + Cl_2 \quad . \quad . \quad (i)$$

takes place, but if the aromatic nucleus is easily chlorinated a further irreversible reaction (ii):

$$Ar{\cdot}NH{\cdot}Ac + Cl_2 \longrightarrow ArCl{\cdot}NH{\cdot}Ac + HCl \quad . \quad . \quad (ii)$$

sets in. By choosing a chloroamine—such as acetylchloroamino-2:4-dichlorobenzene—in which the nucleus is already profoundly substituted by chlorine, the further chlorination of that substance is inhibited, and the action of the free chlorine (ii) is transferred to any other aromatic compound which is present. The method is admirably adapted to the measurement of the speed of interaction, and the influence of the constitution of acylamines on their reactivity has been closely studied.[76] Moreover, the method permits the preparation[77] of chloro-derivatives from substances which are too violently attacked by the usual reagents.

In a new process[78] for preparing aliphatic β-diketones, use has been made of the enhanced reactivity of the acetylenic linking when adjacent to the carbonyl group; thus acetylenic ketones of the type (I) readily unite with secondary amines (as in II), and

$$\underset{\text{(I.)}}{RC{:}C{\cdot}CO{\cdot}R} \qquad \underset{\text{(II.)}}{\begin{matrix} RC{:}CH{\cdot}CO{\cdot}R \\ | \\ NR_2 \end{matrix}} \qquad \underset{\text{(III.)}}{RCO{\cdot}CH_2{\cdot}CO{\cdot}R}$$

when the products are hydrolysed with acid the corresponding β-diketones (III) are formed. A similar reaction may be used to convert[79] $\alpha\beta$-ethylenic ketones (I) into unsaturated alcohols, for the first-named substances form additive products with secondary amines (II), which may be reduced to the secondary alcohols. The

$$\underset{\text{(I.)}}{Me{\cdot}CO{\cdot}CR{:}CH_2} \qquad \underset{\text{(II.)}}{Me{\cdot}CO{\cdot}HCR{\cdot}CH_2{\cdot}NR_2}$$

latter, when treated successively with methyl iodide and silver oxide, yield the ammonium hydroxides (III), which easily decompose with loss of water and tertiary amine, giving the unsaturated alcohol (IV):

$$\underset{\text{(III.)}}{Me{\cdot}CH(OH){\cdot}CHR{\cdot}CH_2{\cdot}NR_2Me{\cdot}OH} \longrightarrow \underset{\text{(IV.)}}{Me{\cdot}CH(OH){\cdot}CR{:}CH_2}$$

A new method of inserting the carboxyl group into complex

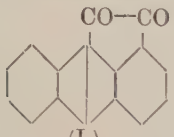
[76] K. J. P. Orton and H. King, *Trans.*, 1911, **99**, 1370; H. King and K. J. P. Orton, *ibid.*, 1377.

[77] H. King, *Proc.*, 1911, **27**, 266.

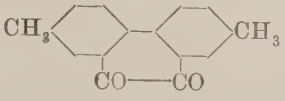
[78] E. André, *Compt. rend.*, 1911, **152**, 525, 1488; *A.*, i, 268, 545.

[79] Farbenfabriken vorm. F. Bayer & Co., D.R.-P. 233519; *A.*, i, 598.

aromatic hydrocarbons[80] is provided by oxalyl chloride. This reactive substance attacks some hydrocarbons, such as anthracene or phenanthrene, when heated alone with them; but the yields of carboxylic acids are better when the cold reagent is employed in presence of aluminium chloride. Under the latter conditions other substances are apt to be formed; thus anthracene yields the new quinone of aceanthrene (I), whilst di-*p*-tolyl gives 2:7-dimethylphenanthraquinone (II):



(I.)



(II.)

The use of the *organo-magnesium* compounds in synthetical work has been as extensive as ever, but the discovery of new methods of applying this reagent has somewhat abated. With regard to the theory of the reagent, some confirmation has been found for the hypothesis[81] that oxonium salts of the type $R_3O{\cdot}X$ are formed as intermediate substances. If such exist, it is to be supposed that in suitable cases some evidence of heterospasis would be found; thus an oxonium salt, $R_2R'O{\cdot}X$, might decompose in either of two ways:

$$R{\cdot}X + R'OR \longleftarrow R_2R'O{\cdot}X \longrightarrow R_2O + R'{\cdot}X.$$

Evidence of this decomposition has been obtained[82] in the case of the interaction of magnesium with propyl iodide and triphenylmethyl ethyl ether in xylene solution.

An interesting study of the application of this reagent to dihalogen derivatives has been made.[83] It is evident that from a normal dihalogen compound (I) a variety of products might be formed, for, on the one hand, if the metal acts merely by removal of halogen, polymethylenes of the structures shown in (II) and (III)

$$\underset{\text{(I.)}}{Br{\cdot}[CH_2]_n{\cdot}Br} \qquad \underset{\text{(II.)}}{\overline{|{-}[CH_2]_n{-}|}} \qquad \underset{\text{(III.)}}{\overline{|{-}[CH_2]_n{-}[CH_2]_n{-}|}}$$

might occur in the final product, whilst on the other, open-chain derivatives such as:

$$\underset{\text{(IV.)}}{BrMg{\cdot}[CH_2]_n{\cdot}MgBr} \quad \text{or} \quad \underset{\text{(V.)}}{BrMg{\cdot}[CH_2]_n\ [CH_2]_n{\cdot}MgBr}$$

might result. In the cases of ethylene and trimethylene bromides the former type of reaction is the more prominent, but it is remark-

[80] C. Liebermann, *Ber.*, 1911, **44**, 202, 1153; *A.*, i, 202, 656.
[81] W. W. Tschelinzeff, *A.*, 1905, i, 40.
[82] G. L. Stadnikoff, *Ber.*, 1911, **44**, 1157; *A.*, i, 435.
[83] J. von Braun and W. Sobecki, *ibid.*, 1918; *A.*, i, 701.

able that with $\alpha\delta$-dibromobutane and the higher members of the series this does not take place, substances of types (IV) and (V) being produced; thus $\alpha\kappa$-di-iododecane yielded eicosane and tetracontane, and $\alpha\epsilon$-dibromopentane yielded *n*-decane, pentadecane, and eicosane mixed with yet higher homologues.

Other applications [84] of this reagent have furnished two new methods of preparing nitriles, which are obtained by treating the magnesium derivative with cyanogen or its chloride.

The employment of peroxides as *oxidising agents* has continued to increase. Among the researches dealing with this type of reagent, that concerning the interaction [85] of organic peroxides with unsaturated compounds is of particular interest. Benzoyl hydroperoxide readily reacts with ethylenic derivatives in neutral solvents, giving excellent yields of the ethylene oxide:

$$C_6H_5\cdot CO\cdot O\cdot OH + >C{:}C< \;=\; C_6H_5\cdot CO_2H + >C\overset{O}{\diagup\diagdown}C<,$$

from which the corresponding glycols may be obtained. At the same time it is shown that even in the case of substances containing conjugated unsaturation, an accurate estimate may be formed of the number of ethylenic groups present in the original compound. Moreover, the character of the unsaturated group may be inferred from the behaviour of the oxide with acid reagents, for those containing the $\cdot CH\overset{O}{\diagup\diagdown}CH_2$ group yield aldehydes, $CHO\cdot CH_2\cdot$, and those containing the structure $\cdot CH\overset{O}{\diagup\diagdown}CH\cdot$ give ketones, $\cdot CH_2\cdot CO\cdot$, by isomeric change in the presence of acids. Other work with this type of reagent has dealt with the interaction of hydrogen peroxide and alkaloïds, those of the morphine group [86] yielding amino-oxides.

With sulphur compounds it has been observed that in the case of thiobenzanilide [87] addition of oxygen to sulphur takes place, whilst with thiophen [88] hydroxy-derivatives of the nucleus are formed.

The formation of ozonides and the decomposition of these by water has been extensively applied to determining the structure of ethylenic compounds, the method being particularly useful in

[84] V. Grignard, *Compt. rend.*, 1911, **152**, 388; *A.*, i, 292.

[85] N. Prileschaéeff, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1387; *A.*, 1910, i, 86, 255.

[86] M. Freund and E. Speyer, *Ber.*, 1910, **43**, 3310; *A.*, i, 76.

[87] E. de B. Barnett, *Proc.*, 1911, **27**, 115.

[88] M. Lanfry, *Compt. rend.*, 1911, **153**, 73, 821; *A.*, i, 740, 1009.

the case of the polymerisation products of divinyl and its derivatives.[89]

A preliminary investigation has been made[90] of the use of silver nitrate as a catalyst in presence of persulphates, and the results give promise of an interesting method of obtaining sensitive oxidation products.

On turning to *reducing agents* it is evident that the method which possesses the greatest interest at the moment is that depending on the contact action of certain metals or their oxides in presence of hydrogen. In view of the thoroughness with which this subject has been treated in the previous report, and of the admirable summary which has been given by Sabatier[91] in an address to the German Chemical Society, the remarks now made need be only few and of a general character. As work proceeds with this method, the possibilities of employing it for selective reduction become more and more apparent. In a comprehensive paper[92] dealing with the behaviour of hydroaromatic compounds in the presence of hydrogen and colloidal palladium, it has been shown that reduction may be carried out under conditions which practically exclude intramolecular rearrangement. Moreover, unsaturated ketones containing more than one ethylenic linking may be completely reduced without interfering with the carbonyl groups. Other work[93] has shown that by choosing suitable conditions the *cyclo*propane system can be guarded from reduction, whilst ethylenic linkings present are removed. It is further evident that the selective action of this type of reagent can be varied by altering the temperature of interaction or the pressure of the hydrogen[94]; thus, when phenanthrene vapour and hydrogen are passed over palladium at 160°, the octahydride is formed, but if reduction is carried out at the ordinary temperature in *cyclo*hexane solution only tetrahydrophenanthrene is obtained. The reduction of phorone[95] serves to illustrate the effect of altering the pressure of hydrogen during the reduction. Using colloidal platinum as the catalyst, a pressure of one and a-half atmospheres confines the reduction to the ethylenic linkings, but with increasing pressure more and more complete interaction is obtained:

[89] C. D. Harries, *Annalen*, 1911, **383**, 157; *A.*, i, 798; S. V. Lebedeff, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 949; *A.*, i, 26.

[90] P. C. Austin, *Trans.*, 1911, **99**, 264.

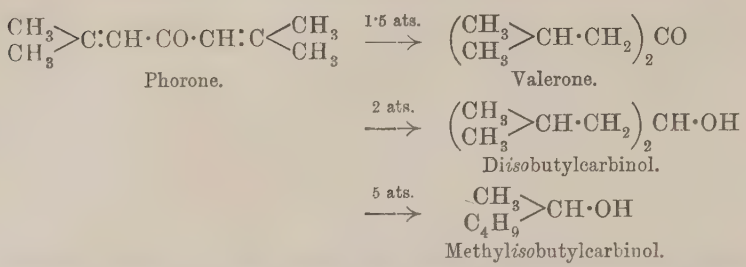
[91] P. Sabatier, *Ber.*, 1911, **44**, 1984; *A.*, i, 702.

[92] O. Wallach, *Annalen*, 1911, **381**, 51; *A.*, i, 469; G. Vavon, *Compt. rend.*, 1911, **152**, 1675; *A.*, i, 657.

[93] L. A. Tschugaeff, *Compt. rend.*, 1910, **151**, 1658; *A.*, i, 72.

[94] P. Breteau, *ibid.*, 1368; *A.*, i, 123.

[95] A. Skita and H. Ritter, *Ber.* 1910, **43**, 3393; *A.*, i, 71.



Active search is being made for other catalysts which might replace the more expensive platinum or palladium, and among those discovered especial mention may be made of copper and its oxide.[96] The experiments with these substances were carried out by heating the unsaturated compound with hydrogen and the catalyst in an iron tube; but the remarkable fact was observed that with tubes of copper no reduction took place, whence it appears that two catalysts should be simultaneously present. In any case, however, copper oxide is not so efficient as nickel oxide.

Attention may be here directed to the interesting fact that the same catalyst obtained in different ways may lead to varying results. A recent example of this behaviour is the reduction of α-pinene with palladium at the ordinary temperature.[97] When the catalyst is prepared from palladium ammonium chloride with formic acid in the presence of alkali, reduction proceeds normally to hydropinene, but with palladium made from palladous chloride and the same reagents, *iso*pinene is formed. This is one of the few cases of intramolecular change which have been observed with this reducing agent, and it is probably due to subsequent oxidation of the hydropinene formed in the preliminary stages of the action.

There is a general desire among organic chemists to explain the action of these catalysts by the formation of some intermediate substance; for example, in the case of nickel [98] it is probable that some unstable hydride is formed, which easily yields hydrogen to substances brought into contact with it. This conception furnishes an explanation of the oxidising power exerted by the metal when heated alone with a saturated substance, for hydrogen and the unsaturated derivative are then formed. In fact, it is probable that during all these catalytic reductions the reverse action [99] takes place at the same time, and in many cases by choosing conditions one or other process may be made to predominate. Many experi-

[96] W. N. Ipatieff, *Ber.*, 1910, **43**, 3387, 3546; *A.*, i, 31, 137.
[97] N. D. Zelinsky, *ibid.*, 1911, **44**, 2782; *A.*, i, 997.
[98] Sabatier, *ibid.*, 1998; *A.*, i, 702.
[99] A. Skita and H. Ritter, *ibid.*, 668; *A.*, i, 272; N. D. Zelinsky and N. Glinka, *ibid.*, 2305; *A.*, i, 870; N. D. Zelinsky, *ibid.*, 3121; *A.*, i, 958.

ments have shown that the presence of oxygen in the nickel employed has a favourable influence on the course of the reduction; this circumstance has been explained by assuming that the water formed from the oxide and hydrogen immediately attacks the reduced nickel with renewed liberation of hydrogen in an active condition. When working with liquids at the ordinary temperature it has been suggested [1] that substances of the following type (I) are

$$\text{(I.)}\quad \begin{matrix} \text{R'CH—CHR'} \\ \diagdown\!\diagup \\ \text{H}_n\text{M(OH)}_m \end{matrix} \longrightarrow \text{R'CH}_2\cdot\text{CH}_2\text{R'} + \text{M(OH)}_m$$

formed, which pass into solution in the colloidal state, and then decompose as indicated, regenerating the oxide and liberating the saturated substance.

More recent research has tended to complicate rather than to simplify the question of the catalytic mechanism. It has been pointed out [2] that all metals which behave as reduction-catalysts contain small quantities of oxygen, and the opinion has been expressed that the various metallic hydrides merely convert this into the hypothetical perhydride of oxygen, OH_4, which then may decompose into oxygen and hydrogen, and so furnish the material either for reduction or for oxidation.

Against this hypothesis the consideration may be offered that any agent which is capable of reducing oxygen to this extent would also probably be sufficiently powerful to reduce unsaturated carbon, so that so far as reduction is concerned the assumption appears to be unnecessary. In the present state of affairs the simpler explanation forms a quite satisfactory working hypothesis, and, in the opinion of the writer, it will be difficult to overthrow without quantitative experiment.

For better illustration of the specific action of contact substances it is necessary to turn to the *interaction of alcohols and acids* in presence of metallic oxides. In decompositions of this type it would be almost impossible, without assuming the formation of derivatives of the catalyst, to give a satisfactory account of the origin of the diverse products. The question has been very carefully studied.[3] When a mixture of an alcohol and an acid are passed over a hot oxide (MO) which functions as the catalyst, four different types of interaction may take place:

I. $\text{MO} + 2\text{R}\cdot\text{CO}_2\text{H} = \text{H}_2\text{O} + (\text{RCO}_2)_2\text{M} = \text{MO} + \text{CO}_2 + \text{H}_2 + \text{R}\cdot\text{CO}\cdot\text{R}.$

II. $\text{MO} + 2\text{C}_n\text{H}_{2n+1}\text{OH} \rightleftarrows \text{H}_2\text{O} + (\text{C}_n\text{H}_{2n+1}\text{O})_2\text{M}.$

III. $\text{M}(\text{OC}_n\text{H}_{2n+1})_2 = \text{MO} + \text{H}_2\text{O} + 2\text{C}_n\text{H}_{2n}.$

IV. $\text{M}(\text{OC}_n\text{H}_{2n+1})_2 + 2\text{R}\cdot\text{CO}_2\text{H} = \text{MO} + 2\text{R}\cdot\text{CO}_2\cdot\text{C}_n\text{H}_{2n+1} + \text{H}_2\text{O}.$

[1] S. Fokin, *J. Russ. Chem. Phys. Soc.*, 1910, **42**, 1074; *A.*, i, 1.

[2] N. D. Zelinsky and N. Glinka, *loc. cit.*

[3] P. Sabatier and A. Mailhe, *Compt. rend.*, 1911, **152**, 358, 494; *A.*, i, 208.

An explanation of the varying results with different acids and catalysts is found on considering these various interactions. Generally speaking, the yield of ester depends on whether the acid readily undergoes the first of these decompositions; if it does not, then ester-formation (IV) predominates, and reactions (I), (II), and (III) are negligible. In the presence of thoria at 400°, acetic acid readily interacts according to (I); hence the amount of ester obtained under these conditions is small, all four types of decomposition then occurring. The yields of ester may be very much improved by choosing an acid, such as benzoic, which does not easily give the ketone decomposition (I); in such a case the formation of esters with fatty alcohols almost accords with theory, being as high as 95 per cent. On the other hand, the same result may be attained by choosing a catalyst, such as titanium oxide at 280—300°, which does not decompose the acid (I); and by adopting this plan good yields of the esters of acetic and other fatty acids may be obtained. Another method of attaining the desired esters is to modify the temperature of interaction; thus with thoria at 150° even formic[4] acid may be esterified.

The catalytic decomposition of esters, which forms the reverse aspect of this question, has also been studied.[5] Hydrolysis of the ester will take place as follows:

$$2R{\cdot}CO_2{\cdot}C_nH_{2n+1} + 2MO = (RCO_2)_2M + (C_nH_{2n+1})_2M,$$

and it is shown that the stability of these products in presence of the catalyst will determine the nature of the ensuing decomposition. According to theory three cases are possible. If the alcohol and acid are equally stable in respect to the catalyst, the ethylenic hydrocarbon and the ketone will be simultaneously produced; if the acid is the less stable, the ketone will appear in larger quantity with the alcohol, and some of the unsaturated compound; whilst if the alcohol is the less stable,[6] the bulk of the product will consist of the ethylenic derivative, and only a small amount of ketone may be formed. In this manner the varying types of decomposition observed with esters in presence of different catalysts may be satisfactorily explained. The discussion of many of these cases would be of interest, but this is precluded by considerations of space and the nature of this report; however, it is hoped that enough has been said to show the state of development which the theory of these catalytic actions has attained during the past year. On the other hand, the practical application of the catalytic method has

[4] P. Sabatier and A. Mailhe, *Compt. rend.*, 1911, **152**, 1044; *A.*, i, 416.
[5] P. Sabatier and A. Mailhe, *ibid.*, 669; *A.*, i, 348.
[6] See W. N. Ipatieff, *Ber.*, 1910, **43**, 3383; *A.*, i, 25.

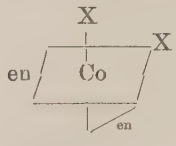
been extended to the preparation of phenolic ethers,[7] amines,[8] and unsaturated hydrocarbons.[9] Finally, it may be remarked that a perusal of the patent literature of the past two or three years will convince the reader of the general value of the process.

J. E. Marsh[10] has obtained liquid compounds of certain halogen double salts with ether. Among the salts which give such liquid compounds are lithium, sodium and potassium mercuri-iodides, lithium mercuribromide, lithium silver iodide, and lithium cuprous iodide. These liquids take up only a limited amount of ether, and are nearly insoluble in excess of ether. The potassium mercuri-iodide compound was mentioned in last year's report.[11] Some of the halogen double salts also bring about a complete mixture of ether and water, forming a homogeneous solution. If these ether-aqueous solutions are warmed, they may separate into two, and even into three, distinct solutions, forming separate layers in a tube, which are permanent if the temperature is kept constant, and become miscible again on cooling. Among the salts which have been found to give ether-aqueous solutions separating into three layers on warming are sodium, potassium, and rubidium mercuri-iodides, ammonium mercuribromide, and lithium mercurichloride. This separation into layers can be explained with the help of the theory of Le Chatelier[12] and of van't Hoff.[13] Ether dissolves potassium mercuri-iodide with evolution of heat; water dissolves it with absorption of heat. Moreover, heat is given out when ether is mixed with the aqueous solution and when water is mixed with the ether solution. Hence on warming the homogeneous solution, it tends to expel ether and water, and also to drive the salt out of the ether into the water solution; thus the three layers consist of a weak ether solution, an ether-aqueous solution, and a strong water solution, the latter containing excess of potassium iodide, since the salt itself is partly separated into its constituents.

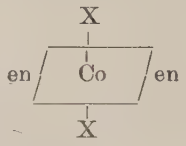
Werner[14] has discovered a remarkable series of group-inversions analogous in some respects to the Walden inversion. These inversions take place among the diethylenediaminecobaltic compounds, and consist in a conversion of the *cis*-form into the *trans*-, and the *trans*-form into the *cis*-. According to Werner's theory, the *cis*- and *trans*-form are represented by the following models, where

[7] A. Mailhe, *Chem. Zeit.*, 1911, **35**, 485.
[8] A. Mailhe, *ibid.*, 1910, **34**, 1173, 1182, 1201.
[9] W. N. Ipatieff, *Ber.*, 1910, **43**, 3383; *A.*, i, 25.
[10] *Trans.*, 1910, **97**, 2293; *Proc.*, 1911, **27**, 328.
[11] *Ann. Report*, 1910, 35.
[12] *Compt. rend.*, 1885, **100**, 441; *A.*, 1885, 473.
[13] *Arch. Néerland*, 1886, **20**, 53.
[14] *Ber.*, 1911, **44**, 873; *A.*, i, 424.

the six groups occupy the angles of an octahedron, of which the cobalt atom occupies the centre:



Cis-form, 1 : 2.



Trans-form, 1 : 6.

$$en = NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2.$$

There are three types of reactions by which the change is brought about: (1) substitution reactions, (2) additive reactions, (3) disruptive reactions. The following examples will serve to illustrate them.

(1) Substitution reactions:

$$\left[\begin{matrix}(1)\ SCN \\ (6)\ Cl\end{matrix} Co\ en_2\right]X + NH_4OH = \left[\begin{matrix}(1)\ SCN \\ (2)\ HO\end{matrix} Co\ en_2\right]X + NH_4Cl.$$

$$\left[\begin{matrix}(1)\ Cl \\ (2)\ Br\end{matrix} Co\ en_2\right]Br + HBr = \left[\begin{matrix}(1)\ Br \\ (6)\ Br\end{matrix} Co\ en_2\right]Br + HCl.$$

(2) Additive reactions:

$$\left[\begin{matrix}(1)\ Cl \\ (6)\ Cl\end{matrix} Co\ en_2\right]Cl + NH_3 = \left[\begin{matrix}(1)\ H_3N \\ (2)\ Cl\end{matrix} Co\ en_2\right]Cl_2.$$

(3) Disruptive reactions:

$$\left[\begin{matrix}(1)\ Cl \\ (2)\ H_3N\end{matrix} Co\ en_2\right](NO_2)_2 = \left[\begin{matrix}(1)\ Cl \\ (6)\ O_2N\end{matrix} Co\ en_2\right]NO_2 + NH_3.$$

$$\left[\begin{matrix}(1)\ H_2O \\ (6)\ H_2O\end{matrix} Co\ en_2\right]Cl_3 = 2H_2O + \left[\begin{matrix}(1)\ Cl \\ (2)\ Cl\end{matrix} Co\ en_2\right]Cl.$$

That we have not to do here with the formation of the only possible isomeride, or even of the most stable isomeride, is shown by the behaviour of the isomerides themselves, for example:

$\left[\begin{matrix}(1)\ Cl \\ (6)\ Cl\end{matrix} Co\ en_2\right]X$ gives with potassium hydroxide $\left[\begin{matrix}(1)\ HO \\ (2)\ H_2O\end{matrix} Co\ en_2\right]X_2$, and

$\left[\begin{matrix}(1)\ Cl \\ (2)\ Cl\end{matrix} Co\ en_2\right]X$ gives with ammonia $\left[\begin{matrix}(1)\ HO \\ (6)\ H_2O\end{matrix} Co\ en_2\right]X_2$.

Sometimes also the reactions result in the formation of a mixture of both the *cis*- and *trans*-isomerides. Further, some groups, such as halogens, NO_2, NCS, enter more readily than others into the octahedral sphere of attraction of the cobalt, and this entrance or exit is dependent also on the nature of the acid group or ion with which the cobalt complex is associated. In reactions of substitution there is evidence that the reagent which is going to bring about the substitution forms, in the first place, an additive

compound with the cobalt complex, an additive compound which it is in some cases possible to isolate; for example, the compound $\left[\begin{matrix}SCN\\Cl\end{matrix}\ Co\ en_2\right]NO_3$ gives with silver nitrate a compound

$$\left[\begin{matrix}SCN\\AgCl\end{matrix}\ Co\ en_2\right](NO_3)_2$$

which is soluble in water and precipitated by nitric acid; on warming the solution, silver chloride is precipitated.

Rings containing six carbon atoms have long been known to unite directly with one another in two ways. In one the rings are united by one carbon atom of each ring, as in diphenyl. In the other the union is effected by means of two carbon atoms common to both rings, as in naphthalene and phenanthrene.

So far, however, no hydrocarbon has been described in which two benzene rings are directly united by the linking of two carbon atoms of one ring to two carbon atoms of another.

Special interest therefore attaches to the preparation of diphenylene, $C_6H_4{:}C_6H_4$,

This was obtained in almost theoretical amount by heating an ethereal solution of 2:2′-dibromodiphenyl with sodium until all action ceased.[15] The constitution of the hydrocarbon follows from its mode of preparation, its molecular weight, and from the fact that it yields phthalic acid when oxidised by chromic acid mixture.

Acetylene is slowly absorbed by iodine at about 150°, and a mixture of two isomeric di-iodides is obtained. This can be separated into a solid and a liquid isomeride.[16] Fumaric acid having been obtained from the solid compound by means of potassium cyanide and hydroxide, it has usually been regarded as the *trans*- or fumaric form, and the liquid isomeride as the *cis*- or maleic form:

H·C·I ‖ I·C·H	H·C·I ‖ H·C·I
Solid acetylene di-iodide (melts at 73°).	Liquid acetylene di-iodide (boils at 185°).

This view has now been confirmed,[17] and it has been shown that solid acetylene di-iodide can be converted into fumaric acid, and its liquid isomeride into maleic acid.

The differences of opinion which show themselves whenever diazo-compounds are under discussion indicate that up to the present no general agreement as to their constitution has been reached.

[15] J. J. Dobbie, J. J. Fox, and A. J. H. Gauge, *Trans.*, 1911, **99**, 683.

[16] E. H. Keiser, *Amer. Chem. J.*, 1899, **21**, 261; *A.*, 1899, i, 398.

[17] E. H. Keiser and L. McMaster, *ibid.*, 1911, **46**, 518; *A.*, i, 949.

Morgan and Miss Micklethwait[18] note that all the available evidence strongly supports the assumption that the diazotisability of a base depends on the association of its amino-group with an unsaturated organic complex. This complex need not necessarily be aromatic or even cyclic, but it is, apparently, essential that it should be unsaturated, for hitherto no amine possessing a fully saturated radicle has ever been diazotised. The existence of a certain degree of residual affinity is a necessary condition for the production of a diazonium salt.

Among aromatic compounds this residual affinity is supplied by the fourth valency of each carbon atom of the six-membered rings. The authors conclude that maximum stability of the diazonium salt results when the residual affinities of the organic radicle and the diazonium complex satisfy each other to the fullest extent.

In an aromatic monodiazonium salt the residual affinity of the nitrogen atoms is available for saturating the six fourth valencies of the carbon atoms.

Acetaldehydephenylhydrazone was first obtained from the interaction of acetaldehyde and phenylhydrazine by E. Fischer, who showed[19] that it could exist in two forms, and possibly in a third.

The so-called β-variety having the lower melting point was obtained by distilling under diminished pressure the original product. This was transformed into the α-variety having a much higher melting point by boiling an alcoholic solution for a few moments with a little sodium hydroxide. When recrystallised under certain undetermined conditions a product of lower melting point, regarded as possibly a third form, was frequently obtained. Lockemann and Liesche some years later[20] carefully examined the compound, and found that it really existed in two modifications: a stable form termed the α-modification melting at 98—101°, and a labile form termed the β-modification melting at 57°. They found that the latter gradually changes into the α-modification, but that the transformation is hastened by the action of bases such as sodium hydroxide or ammonia. The change from the α- to the β-form is effected very rapidly by treatment with aqueous sulphurous acid. These interesting phenomena have been recently re-investigated by E. G. Laws and N. V. Sidgwick.[21] They find that in the preparation from aldehyde and phenylhydrazine a variable mixture of the two modifications is obtained. The α-form (m. p. 98°) is best obtained by carefully crystallising the original material from aqueous alcohol containing a trace of potassium hydroxide, and the

[18] G. T. Morgan and Miss F. M. G. Micklethwait, *Trans.*, 1910, **97**, 2561.

[19] *Ber.*, 1896, **29**, 795; *A.*, 1896, i, 361.

[20] *Annalen*, 1905, **342**, 14; *A.*, 1906, i, 111.

[21] *Trans.*, 1911, **99**, 2085.

β-modification (m. p. 56°) by similar crystallisation from the same solvent containing a trace of sulphur dioxide. Acetaldehydephenylhydrazone thus possesses the remarkable property that either form can be converted into the other almost quantitatively by the action of a mere trace of acid or alkali.

Transformation also is easily brought about without any appreciable alteration in the appearance of the crystals by exposing β- or α-crystals to an atmosphere of ammonia or sulphur dioxide respectively.

No change of optical properties could be recognised when a fairly large crystal of the α-modification was converted into the β-modification under the influence of a drop of acid.

The peculiarity of the isomerism is obviously connected with the very small difference in energy content, and therefore in the relative stability of the two forms. On the other hand, there can be no doubt that the α-form is more stable in presence of alkali and the β- in presence of acid, and that a trace of acid or alkali can bring about a change from one to the other, proceeding through a mass of crystals without their passing into solution. It therefore follows that there is a difference between crystals in contact with acid and crystals in contact with alkali. This can only come about by adsorption of acid or alkali into the crystals, which causes a difference in energy greater than the difference between the two absolutely pure forms.

Distillation in steam or recrystallisation yields an equilibrium mixture of the two forms. There seems to be little ground for the authors' conclusion that the modifications are stereoisomerides.

s-Dichlorocarbamide, $NHCl{\cdot}CO{\cdot}NHCl$, was obtained[22] some years ago by passing chlorine into a cold saturated aqueous solution of carbamide; monochlorocarbamide, $NH_2{\cdot}CO{\cdot}NHCl$, the formation of which must precede that of dichlorocarbamide, has recently[23] been prepared in a similar manner by passing the requisite amount of chlorine into an aqueous solution of carbamide, and cooling in methyl chloride. The compound resembles in properties the more easily prepared *s*-dichlorocarbamide, but is more soluble in water.

It has been shown[24] that when phenylhydrazine is heated under ordinary atmospheric pressure to its boiling point, 241—242°, it decomposes comparatively rapidly into aniline, ammonia, nitrogen, and benzene, thus:

$$2C_6H_5{\cdot}NH{\cdot}NH_2 = C_6H_5{\cdot}NH_2 + NH_3 + N_2 + C_6H_6.$$

[22] F. D. Chattaway, *Proc. Roy. Soc.*, 1908, **81**, 381; *Chem. News*, 1908, **98**, 285; *Trans.*, 1909, **95**, 129.

[23] A. Béhal and A. Detœuf, *Compt. rend.*, 1911, **153**, 681; *A.*, i, 957.

[24] F. D. Chattaway and M. Aldridge, *Trans.*, 1911, **99**, 404.

Other aromatic hydrazines when heated undergo similarly simultaneous oxidation and reduction. As the precise course of any such auto-reduction depends only on the group to which the hydrazine concerned belongs, these interactions may be expressed by general equations.

Primary hydrazines yield a primary amine, nitrogen, ammonia, and a hydrocarbon:

$$2R{\cdot}NH{\cdot}NH_2 = RNH_2 + N_2 + NH_3 + RH.$$

Unsymmetrical secondary hydrazines yield a secondary amine, nitrogen, and ammonia:

$$3RR'N{\cdot}NH_2 = 3RR'NH + N_2 + NH_3.$$

Symmetrical secondary hydrazines yield a primary amine and an azo-compound:

$$2RNH{\cdot}NHR' = RNH_2 + R'NH_2 + RN{:}NR'.$$

Desmotropic Substances.

During the past year our knowledge of this important and interesting group of substances has been considerably enlarged, and, taking a general view of the discoveries made, it may be said that research has proceeded in three chief directions. New experimental processes have been devised for the isolation of desmotropic forms in the pure condition, quantitative methods have been applied to the analysis of equilibrium-mixtures or to determining the speed of interchange of the isomerides, and several new examples of this type of substance have been discovered.

It has long been known that the speed with which equilibrium is attained in allelotropic mixtures is retarded by decrease in temperature, but the logical development of this relation has only recently been realised by Knorr, who has skilfully applied the technique of low temperature work to the isolation of the pure isomeric forms of acetoacetic ester.[25] The ketonic form of acetoacetic ester has been isolated in the crystalline state by cooling to $-80°$ solutions of the ordinary ester in suitable media; but the pure product, which does not exhibit the ferric chloride reaction, can only be preserved at low temperatures. Even at the atmospheric temperature the change into the enolic form begins. To obtain the latter substance the pure sodium salt of the ester is suspended in the cold medium and treated with less than a molecular proportion of dry hydrogen chloride. The difficulty of preparing this isomeride is very much increased by the necessity of performing at the temperature of $-78°$ all operations such as filtration of the

[25] L. Knorr, O. Rothe, and H. Averbeck, *Ber.*, 1911, **44**, 1138, 2767; *A.*, i, 516, 976.

reacting mixture and evaporation of the solvent, for the substance changes into the ketonic form some fifty times more rapidly than it is formed from the latter. It is noteworthy that, in accordance with previous experiments[26] on other types of tautomeric change, the presence of slight impurities emanating from the glass of the vessels employed or from the atmosphere may enormously increase the speed of isomerisation.

The isolation of these isomerides in the pure condition has led to renewed discussion of the composition of the equilibrium mixtures of acetoacetic ester, but the results obtained by different workers are not strictly concordant. The simplest method employed in determining the relative quantities of the isomerides present is to compare[27] the refractive index of the mixture with those of the pure isomerides or artificial mixtures. The results show that the equilibrium mixture in the case of acetoacetic ester contains about 2 per cent. of the enolic isomeride. It is noteworthy that this process is more trustworthy than the previous application of refractive power to the problem, for it does not involve the assumption of a theoretical value for the enolic compound which is certainly inaccurate; moreover, experimental sources of error appear to be fewer than in other methods recently devised for the same purpose.

One of the latter is based on the observation[28] of Lapworth that the enolides very rapidly react with bromine, forming the brominated ketones, and it is shown[29] that the latter may be quantitatively reduced to ketones by hydriodic acid, iodine being liberated. Accordingly, to determine the quantity of enolic isomeride present in a sample of the ester, a cold solution of the latter is mixed with an alcoholic solution of bromine, β-naphthol being immediately added to remove excess of this halogen; potassium iodide is then added, and, the solution having been warmed, the free halogen is titrated in the usual manner. Experiments with acetoacetic ester gave results showing the presence of about $7\frac{1}{2}$ per cent. of the enolic isomeride. There is no doubt that the chief source of error in this process is the transformation of the ketonic into the enolic form after the latter has been removed from the equilibrium mixture by conversion into bromo-ketone. It is true that the process can be very rapidly performed, and that the author of the method estimates the maximum error from the source mentioned at about one-fifth per cent.; but it nevertheless seems impossible accurately to gauge the error thus introduced until blank experiments have

[26] T. M. Lowry, *Trans.*, 1903, **83**, 953.

[27] L. Knorr, O. Rothe, and H. Averbeck, *loc. cit.*

[28] A. Lapworth, *Trans.*, 1904, **85**, 30.

[29] K. H. Meyer, *Annalen*, 1911, **380**, 212; *A.*, i, 350; K. H. Meyer and P. Kappelmeier, *Ber*, 1911, **44**, 2718; *A.*, i, 832.

been made to find the rate of enolisation in presence of the same concentration of free hydrobromic acid. In fairness, however, it must be added that a recalculation of the data obtained by Hantzsch [30] in his spectroscopic investigation is stated [31] to lead to the same result, but it is impossible to form an estimate of the weight of this evidence until fuller details are published.

Yet a third method [32] has been proposed for the estimation of the relative amounts of the tautomeric forms present in a mixture, and, although it has not yet been applied to the case of acetoacetic ester, it is worthy of description. Use is made of the fact that the colour produced by the interaction of ferric chloride and an enolic compound reaches a maximum intensity when equimolecular proportions of the reagents are present, the interaction being as expressed by the following equation:

$$R{\cdot}OH + FeCl_3 = FeCl_2{\cdot}OR + HCl.$$

Standard solutions are made from the pure enolide and the requisite proportions of ferric chloride, and these are compared in a colorimeter with solutions of the desmotropic mixture containing a corresponding amount of the iron salt. In this connexion it is interesting to notice that Knorr has succeeded in obtaining the pure ferric salts of the enolides—$(RO)_3Fe$—by decomposing the sodium derivatives with ferric chloride in ethereal solution; these may be employed in preparing the standard solution of ferric mono-enolides by mixing them in suitable solvents with ferric chloride and hydrochloric acid in the proportions required by the following equation:

$$Fe(OR)_3 + 2FeCl_3 + 3HCl = 3FeCl_2{\cdot}OR + 3HCl.$$

This scheme of estimating the enolic isomeride has been applied with interesting results to methyl mesityl-oxide-oxalate in solution and in the fused condition.

Although it is evident that the complete investigation has not yet been published, in criticism it may be submitted that the method is probably limited in application to substances, such as that mentioned above, which are not too rapidly enolised. Experiments from another source with acetoacetic ester indicate that ferric chloride acts on that substance as a powerful enolising agent [33]; at the same time it is noteworthy that a complete study of the conditions has shown that the process of enolisation involves a unimolecular reaction—a result in harmony with the conclusion

[30] K. H. Meyer, *loc. cit.*

[31] A. Hantzsch, *Ber.*, 1910, **43**, 3049; *A.*, 1910, i, 811.

[32] L. Knorr and H. Schubert, *ibid.*, 1911, **44**, 2772; *A.*, i, 948.

[33] K. H. Meyer, *ibid.*, 2725; *A.*, i, 833. See, however, A. Hantzsch and C. H. Desch, *Annalen*, 1902, **323**, 1; *A.*, 1902, i, 708.

previously attained by Lapworth in studying the action of bromine with these substances.

Other enolising agents have been studied, and attention may be directed to the influence of iodine in presence of mineral acids. Experiments[34] made with this reagent and ketones of the structure $R{\cdot}CO{\cdot}C_nH_{2n+1}$ have shown that the rate of enolisation depends on the nature of the alkyl groups present. In comparison with those of normal structure the *iso*alkyl grouping exerts a marked restraining influence; indeed, in general character the relations appear to be similar to those obtained by other methods of measuring the activity of the carbonyl group, such as the rate of addition of bisulphite[35] and of oxime formation,[36] and the selective absorption of light.[37]

The question of the influence of the solvent has also received attention. Experiments[38] made with the ethyl ester of 5-hydroxy-1-phenyltriazolecarboxylic acid (I):

$$NPh\langle\begin{matrix}C(OH)\\N{=}N\end{matrix}\rangle C{\cdot}CO_2Et \rightleftharpoons NPh\langle\begin{matrix}CO\\N{:}N\end{matrix}\rangle CH{\cdot}CO_2Et$$

(I.)

in numerous solvents show that the velocity of isomerisation of this substance and the state of equilibrium do not depend on the dielectric constant of the solvent, but are influenced by the relative solubilities of the isomerides. Without the fortunate discovery of the desmotropic pair:

$$\underset{\text{Neutral.}}{NPh\langle\begin{matrix}C(NH_2)\\N{=}{-}N\end{matrix}\rangle C{\cdot}CO_2Et} \rightleftharpoons \underset{\text{Acid.}}{NH\langle\begin{matrix}C(NHPh)\\N{=}{=}N\end{matrix}\rangle C{\cdot}CO_2Et}$$

ethyl 5-amino-1-phenyltriazolecarboxylate and ethyl 5-anilinotriazolecarboxylate, some difficulty would have been experienced in obtaining isomerides of a nature permitting the accurate determination of this influence. With the substances in question it was found that the specific influence of a solvent on the equilibrium is a function of the solubility of the reacting substances, and it is remarkable that this relation has been already deduced by van't Hoff from theoretical premises. Expressing this law in general terms it may be said that two isomerides which are mutually interconvertible attain equilibrium in any given solvent when the relation between the ratio of their concentrations and the ratio of their solubilities reaches a certain value; the latter is called the absolute

[34] H. M. Dawson and R. Wheatley, *Trans.*, 1910, **97**, 2048; H. M. Dawson and H. Ark, *ibid.*, 1911, **99**, 1740.

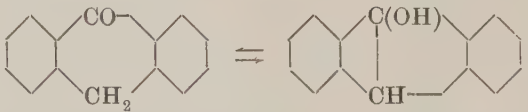
[35] A. W. Stewart, *ibid.*, 1905, **87**, 185. [36] *Ibid.*, 410.

[37] A. W. Stewart and E. C. C. Baly, *ibid.*, 1906, **89**, 489.

[38] O. Dimroth, *Annalen*, 1911, **377**, 127; *A.*, ii, 31.

equilibrium constant, and it is independent of the nature of the solvent. Assuming the truth of this law, further deductions may be made concerning the velocity of change of an isomeride; it then appears that this is either inversely proportional to the solubility of the reacting isomeride or directly proportional to the solubility of the isomeride which is being formed; but it must be observed that accurate experimental data in support of this relation are still wanting. The influence of concentration of the equilibrium of acetoacetic ester in various solvents has been examined [39] with the aid of the titrimetric process described in a foregoing paragraph. The results indicate that the enolic form of the ester present in solution increases as dilution proceeds, whence it follows that the equilibrium depends on the concentration. An attempt to explain this circumstance has been made by taking into consideration the fact that the solvent varies during the series of measurements, being composed of varying amounts of ester and pure solvent. To harmonise the results with the theory deduced from the behaviour of the triazole derivatives it seems necessary to assume that addition of the ester increases the solubility of the ketonic form, and so augments the proportion of that isomeride; but experiments to verify this assumption have not yet been made.

In concluding this short review of new research dealing with desmotropic substances, mention may be made of the isolation of the isomeric forms of some of the more common representatives of this class. The methyl ester of benzoylacetic acid [40] when cooled to $-78°$ yields the crystalline enolic isomeride, and not, as with acetoacetic ester, the ketonic form. The latter, however, is rapidly formed from the enolide at the atmospheric temperature, equilibrium being reached with varying speeds according to the nature of the glass in which the substance is contained. Also acetylacetone yields the crystalline enolide, which likewise undergoes rapid ketonisation. Other work has dealt with anthranol,[41] from which the two desmotropic forms:



(I.) (II.)

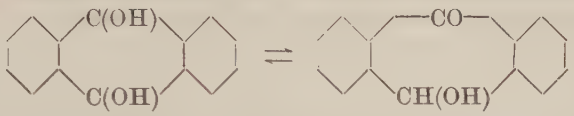
have now been isolated. The substance, which is obtained by reducing anthraquinone with acid reagents, appears to be the pure ketonic isomeride, anthrone (I); but when the ice-cold alkaline solution is mixed with acid, the phenolic derivative, anthranol (II),

[39] K. H. Meyer and P. Kappelmeier, *loc. cit.*

[40] L. Knorr, *Ber.*, 1911, **44**, 2767 ; *A.*, i, 976 ; K. H. Meyer, *ibid.*, 2729 ; *A.*, i, 865.

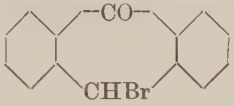
[41] K. H. Meyer, *Annalen*, 1911, **379**, 37 ; *A.*, i, 194.

is obtained in the pure condition. In suitable solvents an equilibrium between these substances may be established. A similar pair of isomerides having the constitution of anthraquinol (III)



(III.) (IV.)

and hydroxyanthrone (IV) have also been obtained. The former is yielded by the interaction of anthraquinone with alkaline reducing agents, and the latter by warming bromoanthrone (V) with aqueous



(V.)

acetone. The velocity of interconversion of these isomerides is very small, but with catalytic agents such as alkali hydroxide it assumes a very high value, the equilibrium being greatly in favour of the dihydroxy-derivative. The isolation of these desmotropic pairs affords some information on the question of tautomerism in the phenols. The assumption made by Thiele that the high reactivity of the phenols is due to change into the ketonic form seems to be contradicted by the behaviour of these compounds, for in the two pairs examined the phenolic derivative is the more reactive isomeride.

Polymerisation of Unsaturated Substances and Some Photochemical Changes.

In view of the probability that polymerisation may take some part in the natural synthesis of complex substances, it may be of interest to review the results of recent researches on this subject, especially since in some cases the effect in question has been produced by the aid of light. Considering the novelty of the subject, the researches carried out during the past year have been relatively numerous, and it is obvious to suggest that this sudden growth is due to the stimulus given by recent experiments on the formation of caoutchouc and similar substances.

The polymerisation of unsaturated substances may be effected by heat or by the influence of light, the ultra-violet rays being particularly efficient; but with either reagent the effect may be reversed. The temperature, and no doubt also the pressure, at which the condensation is carried out influences the character of the products, although the nature of the latter does not depend

on the period of heating. In most cases a mixture of complex substances is formed, and for obvious reasons attention has been mainly directed to the simpler of these.

It seems impossible in the present state of affairs to lay down any comprehensive rules governing the structure of the products obtained from these intermolecular actions, but generally speaking it may be said that cyclic compounds are produced. However, substances containing the open-chain structure have been occasionally observed; for example, the $\alpha\beta$-unsaturated ketone, methyleneacetone (I), on being heated [42] yields the octenedione (II), whilst

$$\underset{\text{(I.)}}{CH_2{:}CH{\cdot}CO{\cdot}CH_3} \qquad \underset{\text{(II.)}}{CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH{:}CH_2}$$

$$\underset{\text{(III.)}}{CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}OH}$$

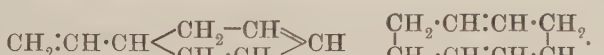
if water and alkali carbonate are present the octadionol (III) is obtained.

With ethylenic compounds, such as the derivatives of cinnamylidene and of diallyl, it appears that mild conditions of polymerisation tend to produce four- and eight-membered cyclic systems, whilst more intense conditions yield substances containing the six-membered arrangement. To illustrate this rough generalisation the following researches may be quoted. Numerous experiments have shown that cinnamic [43] and *allo*-cinnamic [44] acids are converted by the influence of light into α- and β-truxillic acids which contain the four-membered ring; but it has now been observed [45] that prolonged heating of ethyl cinnamate yields the ester of the six membered polycinnamic acid:

$$\begin{array}{l} CO_2Et{\cdot}CH{\cdot}CHPh{\cdot}CH{\cdot}CO_2Et \\ \quad\quad\quad\

phenone,[47] cinnamylidenemalonic [48] and α-methylcinnamylideneacetic acids.[49] The more violent conditions of polymerisation have not yet been applied to the latter group of compounds. The formation of cyclic compounds has also been observed in the polymerisation [50] of ethylene under pressure at high temperatures, which furnishes a product consisting chiefly of polymethylenes, accompanied by paraffins and more complex ethylenic hydrocarbons. Since independent experiment has established the fact that the cyclic arrangement is prone to decomposition under these conditions, it appears probable that the formation of these open-chain derivatives is due to secondary decomposition of the parental polymethylenes.

The question of the relation between the conditions of polymerisation and the nature of the products has been more carefully studied [51] with derivatives of divinyl which contain a conjugated system of ethylenic linkings. These substances yield mixtures of a *cyclo*hexene derivative and a resinous compound, which contains the *cyclo*octadiene system, divinyl, for example, giving ethenyl*cyclo*hexene (I) and the polymeric derivative of *cyclo*octadiene (II):



(I.) (II.)

In this instance and those of isoprene and di*iso*propenyl it has been found that the milder conditions, such as a relatively low temperature or under the influence of light, favour the production of the eight-membered ring, whilst higher temperatures augment the quantity of the *cyclo*hexene derivative. From the numerous data available it seems that the *cyclo*butane ring is not formed from substances containing a system of conjugated ethylenic linking; but it may be remarked that Thiele's hypothesis adds weight to the supposition that this ring may be formed by intramolecular condensation under conditions which have not yet been realised in experiment. It appears, moreover, that the *cyclo*butane system is easily formed from hydrocarbons of the peculiar allene type, the condensation being as usual intermolecular.[52] Experiments with *as*-dimethylallene (I) yielded two isomeric derivatives of *cyclo*butane (II and III), together with dipentene and other more complex substances:

[47] H. Stobbe and C. Rücker, *Ber.*, 1911, **44**, 869; *A.*, i, 385.
[48] C. N. Riiber, *ibid.*, 1902, **35**, 2411; *A.*, 1902, i, 617.
[49] A. L. Macleod, *Amer. Chem. J.*, 1910, **44**, 331; *A.*, 1910, i, 845.
[50] W. N. Ipatieff, *Ber.*, 1911, **44**, 2978, 2987; *A.*, i, 937.
[51] S. V. Lebedeff, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 949; *A.*, i, 26; see also D.R.-P. 235686; *A.*, i, 1003.
[52] S. V. Lebedeff, *ibid.*, 1911, **43**, 820; *A.*, i, 774.

$CH_2{:}C{:}CMe_2$ (I.)

$\begin{matrix} CH_2{\cdot}C{:}CMe_2 \\ | \\ CH_2{\cdot}C{:}CMe_2 \end{matrix}$ (II.)

$\begin{matrix} CH_2{-}C{:}CMe_2 \\ | \\ CMe_2{\cdot}C{:}CH_2 \end{matrix}$ (III.)

The polymerisation products containing the *cyclo*octadiene arrangement exhibit physical and chemical properties which are similar to those of the natural caoutchouc, and hence especial attention has been paid to the conditions that govern their formation. The caoutchoucs derived from isoprene, divinyl, and dimethylbutadiene are best prepared by heating these hydrocarbons in sealed vessels without the presence of a solvent at temperatures near 100° for several days,[53] only slightly different conditions being required in each case to obtain a maximum yield of the product. The caoutchoucs obtained by this method of polymerisation have been termed the "normal caoutchoucs," for investigation of their ozonides shows that they are analogous with the natural product. However, the diozonides obtained from these synthetic caoutchoucs are not homogeneous, for they may be resolved into two isomerides of different solubility, the more soluble being present only in small amount. On being decomposed with water these isomerides yield different products, which may be interpreted as indicating that the parental hydrocarbons differ from one another by the relative situation of the ethylenic linkings in the octadiene complex; for example, since the less soluble ozonide obtained from isoprene–caoutchouc breaks down into lævulaldehyde, the hydrocarbon may be regarded as a derivative of the dimethyloctadiene shown in the following formula (I), whilst the more soluble isomeride is probably

$\begin{matrix} CH_2{\cdot}CH{:}CMe{\cdot}CH_2 \\ | \quad\quad\quad | \\ CH_2{\cdot}CMe{:}CH{\cdot}CH_2 \end{matrix}$ (I.)

$\begin{matrix} CH_2{\cdot}CH{:}CMe{-}{-}CH \\ | \quad\quad\quad\quad\quad || \\ CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH \end{matrix}$ (II.)

derived from some such system as that shown in formula (II), for it yields methylglyoxal on treatment with water. The polymerisation of these unsaturated hydrocarbons may be effected at lower temperatures by the influence of metallic sodium, but the products, although of similar physical character, do not exhibit the same chemical behaviour as the normal caoutchoucs. For the present their nature remains undetermined.

The production of isoprene and its congeners is of technical importance in the preparation of a synthetic caoutchouc, and many experiments have been recently made on that question. Among the methods devised during the past year for the production of isoprene, that originating with acetone[54] deserves especial notice. With the aid of magnesium ethyl bromide, acetone is converted into *tert.*-amyl

[53] C. D. Harries, *Annalen*, 1911, **383**, 157; *A.*, i, 798.

[54] C. D. Harries, *loc. cit.*

alcohol (I), and thence into trimethylethylene (II). The dibromide of the latter (III), when allowed slowly to drop on to hot soda-lime

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}C_2H_5\\OH\end{matrix} \qquad \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{:}CH\cdot CH_3 \qquad \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CBr\cdot CH\cdot CH_3$$

(I.) (II.) (III.)

of suitable character, furnishes excellent yields of the required hydrocarbon. Another noteworthy method [55] consists in passing the vapours of dipentene over a spiral of metallic wire which is heated with the electric current, whilst a patented method applies the process of exhaustive methylation to $\alpha\delta$-diaminobutane and its derivatives.[56]

The study of the condensation of keten [57] and its derivatives [58] has yielded further interesting data on the question of polymerisation. The extreme ease with which these substances polymerise and depolymerise might give rise to the suspicion that the bimolecular compounds are merely physical aggregates of the simpler molecules, but this is negatived by interaction with certain reagents which yield derivatives of the diketomethylene group, $\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot$, thus proving the presence of the *cyclo*butanone structure.

Many of the simpler ketens yield the *cyclo*butane derivatives when kept at the ordinary temperature; in the case of keten itself the polymerisation may proceed further to the six-membered system of dehydracetic acid, but this does not appear to take place so easily with the substituted compounds. The ease with which the *cyclo*butane ring is broken by the aid of heat is remarkable, for simple distillation of the polymeride renders an almost theoretical yield of the keten. Use has been made of this tendency to depolymerise in obtaining some derivatives of keten which only appear as polymerides in the usual methods of preparation. In this manner ethyl ethylketencarboxylate has been isolated, but it can be preserved only at low temperatures. With this substance the temperatures of polymerisation and depolymerisation seem to lie close together:

$$\begin{matrix}CO_2Et\cdot CEt{:}CO\\CO{:}CEt\cdot CO_2Et\end{matrix} \rightleftharpoons CO_2Et\cdot \underset{\displaystyle CO-}{\overset{\displaystyle |}{C}}Et\cdot CO\cdot CO_2Et.$$

Taking into account the general behaviour of substances which form cyclic carbon compounds on polymerisation, the general rule might be framed that those cyclic systems which are formed more

[55] C. D. Harries and K. Gottlob, *Annalen*, 1911, **383**, 228; *A.*, i, 798; H. Staudinger and H. W. Klever, *Ber.*, 1911, **44**, 2212; *A.*, i, 731.

[56] D.R.-P. 231806.

[57] Miss F. Chick and N. T. M. Wilsmore, *Trans.*, 1910, **97**, 1978.

[58] H. Staudinger, *Ber.*, 1911, **44**, 521; 1909, **42**, 4908; *A.*, i, 306; 1910, i, 89.

easily are the more prone to decompose. It seems, however, that this rule cannot be applied to all cyclic substances, for exceptional cases are met with in other products formed from ketens by similar processes; for example, ketones unite with certain ketens,[59] giving β-lactones, which decompose on heating into these components or into carbon dioxide and the ethylene derivative:

$$\begin{matrix} CR_2{:}CO \\ CR_2{:}O \end{matrix} \rightleftharpoons \begin{matrix} CR_2{\cdot}CO \\ | \quad | \\ CR_2{\cdot}O \end{matrix} = \begin{matrix} CR_2 \\ \| \\ CR_2 \end{matrix} + CO_2.$$

With these substances ring-formation proceeds with difficulty, and decomposition occurs easily. On the other hand, the β-lactam which is easily formed from diphenylketen and benzophenoneanil [60]:

$$\begin{matrix} CPh_2{\cdot}CO \\ | \quad | \\ CPh_2{\cdot}NPh_2 \end{matrix} \rightleftharpoons \begin{matrix} CPh_2{:}CO \\ CPh_2{:}NPh \end{matrix}$$

is not very easily split into the components.

In addition to those performed with ethylenic derivatives, experiments have been made on the behaviour of other types of compounds in the presence of light. The majority of the researches carried out on these lines during the past year have dealt with the reactions of ketones with various substances. In these interactions it is rare to find a homogeneous product, for the reacting substances frequently undergo decomposition. However, it may be stated as a general rule that ketones yield a compound of the "hydrol" type if a substance containing the available hydrogen is present:

$$CR_2{:}O + HR' = CR_2{<}\begin{matrix} OH \\ R' \end{matrix}.$$

The peculiarity of the influence of light on these interactions is the unexpected activity which it confers on certain methylene groups; for example, those contained in ethers,[61] alcohols,[62] esters,[63] and acids.[64] With ketones these substances yield the following types of compounds:

$$CPh_2{<}\begin{matrix} OH \\ CHPh{\cdot}CO_2H' \end{matrix} \qquad CPh_2{<}\begin{matrix} OH \\ CHPh{\cdot}OAc' \end{matrix}$$

$$CPh_2{<}\begin{matrix} OH \\ CHMe{\cdot}OEt' \end{matrix} \qquad CMe_2{<}\begin{matrix} OH \\ CHMe{\cdot}OH' \end{matrix}$$

A similar class of product has been obtained from phenanthrene-

[59] H. Staudinger, *Ber.*, 1908, **41**, 1355; *A.*, 1908, i, 410; *Annalen*, 1911, **380**, 243; *A.*, i, 459.

[60] H. Staudinger, *Ber.*, 1911, **44**, 365; *A.*, i, 215.

[61] G. L. Ciamician and P. Silber, *ibid.*, 1354; *A.*, i, 650.

[62] *Ibid.*, 1280; *A.*, i, 513.

[63] E. Paternò and G. Forli-Forti, *Gazzetta*, 1910, **40**, ii, 332; *A.*, i, 66.

[64] E. Paternò and G. Chieffi, *ibid.*, 321; *A.*, i, 65.

quinone and various aldehydes,[65] the interaction proceeding as follows:

$$CO\cdot CO + CHO\cdot Ph = \begin{matrix} C & = & C \\ | & & | \\ OH & & O\cdot COPh \end{matrix}$$

In all these cases subsidiary products are formed, which are ultimately due either to polymerisation or to decomposition of one of the reagents. If ethers, alcohols, or esters are employed, considerable reduction of the ketone is apt to take place, the phenomenon being undoubtedly due to the nascent hydrogen which is formed when these substances are submitted[66] to the influence of light.

Some very interesting experiments have been made on the transformation of ethylenic isomerides by the influence of light. From the numerous data now available it seems that the process may be generally applied[67] to the preparation of the unstable isomerides of low melting point from the more stable. In no case, however, is the transformation complete, since an equilibrium is established; in fact, there is no reason to doubt that the process is reversible, for with many pairs of isomerides the change has at one time or another been realised[68] in both directions. So general does this photochemical process appear to be, that it has been recommended as a means of deciding whether a pair of isomerides are stereochemically related. The application of the method to coumaric and coumarinic acids has resulted in favour of this relation between the two series. Also, with oximes the conversion of *syn-* into *anti-*isomerides, and vice versa, has been observed.

Some of these observations are of particular interest in their bearing on the attractive hypothesis[69] that the change of one stereoisomeride into the other takes place through the intermediate synthesis of a tetramethylene derivative, which ultimately breaks down in such a way as to yield the latter. One of the chief difficulties which stands in the way of this hypothesis has arisen from the circumstance that in the few cases in which the cyclic product has been isolated this has been too stable to permit the assumption of spontaneous decomposition. The objection is now somewhat weakened by the discovery of extremely unstable derivatives of tetramethylene, although it has not yet been shown that light can effect the requisite depolymerisation.

There is no doubt that a more intimate knowledge of the processes

[65] H. Klinger and W. Roerdansz, *Annalen*, 1911, **382**, 211; *A.*, i, 633.

[66] D. Berthelot and H. Gaudechon, *Compt. rend.*, 1911, **153**, 383; *A.*, ii, 835.

[67] R. Stoermer, *Ber.*, 1911, **44**, 637; *A.*, i, 295; 1910, i, 114.

[68] For example, fumaric and maleic acids: G. L. Ciamician and P. Silber, *ibid.*, 1903, **36**, 4266; *A.*, 1904, i, 161; R. Stoermer, *loc. cit.*

[69] A. W. Stewart, *Proc.*, 1905, **21**, 73.

which occur during these photochemical interactions can only be attained by quantitative experiment. Important researches of this type have been carried out within a recent period.

The photochemical transformation of maleic into fumaric acid in presence of small quantities of bromine has been quantitatively studied.[70] One of the more important results of these experiments is the proof that the reaction is unimolecular. Moreover, the velocity of inversion seems independent of the temperature, and when equilibrium is attained the percentage of fumaric acid present is approximately proportional to the amount of bromine taken. Unlike some other photochemical interactions the conversion of maleic into fumaric acid does not continue after the stimulating source of light has been removed. This peculiar after-effect has been observed in the photobromination of toluene, and the cause has now been revealed[71] by a series of exhaustive experiments. These show that the after-effect is caused by the presence of atmospheric oxygen, which forms a catalyst, probably an oxide of bromine, by combination with the halogen present.

Bromination of toluene in the side-chain may be accomplished even in the dark with the aid of this catalyst; in fact, if ozonised air is passed into the unilluminated bromination mixture the interaction is violent; thus ozone may be used with advantage as a "halogen carrier" for substitution in the side-chain of aromatic compounds, and in this respect it is unique. The quantitative study of the photobromination of these substances has hitherto been rendered impossible by the after-effect in question; but the disturbance may be eliminated by the addition of a very small amount of iodine, which decomposes the unstable catalyst. Using this precaution, measurements were obtained which show that the interaction is unimolecular.

Carbohydrates and Allied Substances.

During the past year the chemistry of the aldoses has been considerably developed, but mainly along the lines laid down by the pioneers of this work. The chief difficulty which stood in the way of the expansion of research in this direction was the scarcity of materials from which further syntheses might be started; but the recent discovery of some of this material in natural products has removed the obstacle, and the opportunity has been seized; thus, of the sixteen possible methylpentoses, eight are now known, whilst the group of hexoses has been almost completed by the discovery

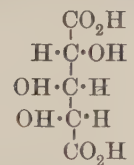
[70] L. Bruner and M. Królikowski, *Bull. Acad. Sci. Cracow*, 1910, 192; *A.*, i, 9.
[71] L. Bruner, S. Czarnecki, and Z. Lahociński, *ibid.*, 23, 516, 560; *A.*, i, 242.

of *d*-allose and *d*-altrose, only the lævo-isomerides of these sugars being required to complete the group.

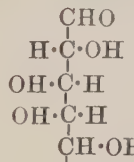
Very interesting experiments have been performed on the synthesis of carbohydrates from simple substances by means of ultra-violet light or sunlight; for instance, an alkaline solution of glycerol is found [72] to contain α-acrose after being exposed to ultra-violet light in the presence of air; and the important observation has been made [73] that under the influence of these rays carbon dioxide and hydrogen yield carbohydrates, but only when the latter-named reagent is in the nascent condition. An aqueous solution of formaldehyde, when subjected to the action of ultra-violet rays, furnishes [74] a volatile substance of reducing properties which appears to be glycollaldehyde; and other experiments [75] with formaldehyde in the presence of oxalic acid lead to the isolation of a crystalline reducing sugar, which resembles sorbose. The study of the reverse aspect of this question has shown that in aqueous solution carbohydrates are decomposed by ultra-violet light. The few experiments which have been made seem to show that with polysaccharides a preliminary hydrolysis takes place,[76] the simpler sugars being then degraded to various products.

Methylpentoses.—A very thorough investigation [77] of the hydrolytic products obtained from the complex glucoside convolvulin has shown that this substance contains no less than three methylpentoses, namely, rhamnose, rhodeose, and *iso*rhodeose. Cautious hydrolysis of the glucoside with aqueous barium hydroxide yields convolvulinic acid, α-methylbutyric acid, and purgic acid; the first-named of these acids yields on further hydrolysis with mineral acid a mixture of rhamnose and rhodeose, whilst from the last-named *iso*rhodeose is obtained.

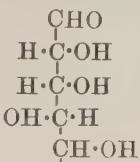
The configuration of rhodeose has been determined by oxidising the lactone of rhodeonic acid. Using nitric acid as the oxidising



l-Trihydroxyglutaric acid.



(I.)



(II.)

[72] H. Bierry and V. Henri, *Compt. rend.*, 1911, **152**, 535; *A.*, i, 255.

[73] J. Stoklasa and W. Zdobnický, *Biochem. Zeitsch.*, 1911, **30**, 433; *A.*, i, 178.

[74] R. Pribram and A. Franke, *Ber.*, 1911, **44**, 1035; *A.*, i, 420.

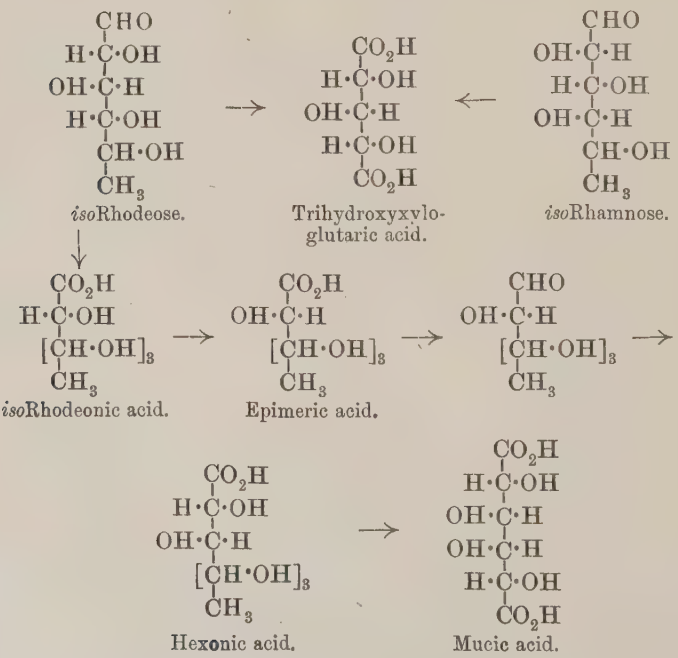
[75] G. Inghilleri, *Zeitsch. physiol. Chem.*, 1911, **71**, 105; *A.*, i, 354.

[76] Compare L Massol, *Compt. rend.*, 1911, **152**, 902; *A.*, i, 356; H. Bierry, V. Henri, and A. Ranc, *ibid.*, 1629; *A.*, i, 524.

[77] E. Votoček, *Ber.*, 1910, **43**, 476; *A.*, 1910, i, 274.

agent, *l*-trihydroxyglutaric acid was obtained, whence it is evident that the aldose must be represented by either of two alternative configurations; but since rhodeitol, the corresponding alcohol, is not attacked by the sorbose-bacterium, it appears that the former of these is correct. This deduction is confirmed by submitting the sugar to the cyanohydrin reaction, and subsequently oxidising the rhodeohexonic acids then obtained. It will be seen that if formula (I) were correct, mannosaccharic and saccharic acids would then be formed, whilst the latter alternative demands the production of mucic and talomucic acids. Actually saccharic acid was isolated, and no trace of mucic acid could be detected in the oxidation product of the rhodeohexonic acids. It may also be observed that the rotatory power[78] of rhodeonolactone is in harmony with this configuration.

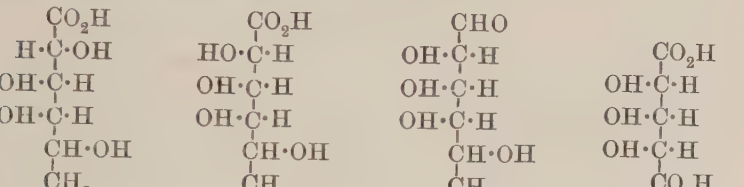
*iso*Rhodeose[79] is evidently the optical antipode of *iso*rhamnose, for apart from the fact that this is indicated by the physical properties of the sugar and its derivatives, chemical evidence leads to the same conclusion. When oxidised with nitric acid, *iso*rhodeose furnishes the inactive trihydroxyxyloglutaric acid:



[78] C. S. Hudson, *J. Amer. Chem. Soc.*, 1911, **33**, 405; *A.*, i, 355.
[79] E. Votoček, *Ber.*, 1911, **44**, 819; *A.*, i, 354.

Moreover, on converting *iso*rhodeonic acid into the epimeric[80] acid by heating with pyridine, and applying to the product Fischer's series of reactions—reduction, addition of hydrocyanic acid, and re-oxidation—mucic acid is obtained. The bearing of this fact on the configuration of *iso*rhodeose is explained by the accompanying formulæ. The evidence in favour of this structure is completed by the fact that the methyltetrose, obtained by degradation of *iso*rhodeose, on being oxidised,[81] yields *l*-tartaric acid.

By heating rhodeonic acid with pyridine in aqueous solution the isomeric *epi*rhodeonic acid has been obtained,[82] and when the lactone of this acid was reduced in the usual manner a new methylpentose, *epi*rhodeose, was formed:



Rhodeonic acid. *epi*Rhodeonic acid. *epi*Rhodeose. Trihydroxyriboglutaric acid.

This sugar has not yet been obtained in the crystalline state; it furnished the same phenylosazone as that given by rhodeose, and on oxidation it was converted into trihydroxyriboglutaric acid, which, somewhat remarkably, was isolated as a weakly active lactone.

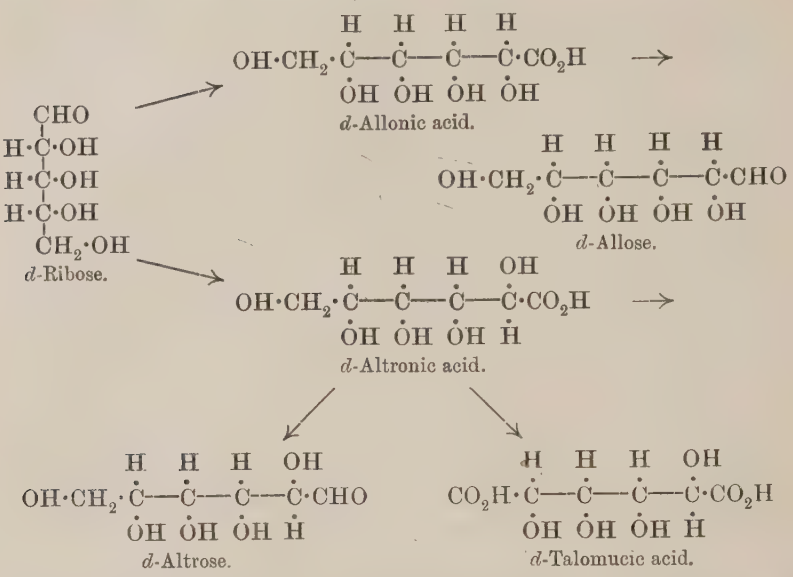
Hexoses.—The discovery that *d*-ribose is a component of many nucleosides has led to the accumulation of a considerable quantity of this substance; thus the preparation of the corresponding hexoses by the cyanohydrin process has come within the range of experiment. When *d*-ribose was submitted[83] to this reaction, a mixture of two hexonic acids was obtained, and these were separated by means of their calcium salts. The less soluble, which was named *d*-altronic acid, must correspond with the configuration shown in the following scheme, for it gives talomucic acid on oxidation:

[80] It has been proposed (Votoček, *loc. cit.*) to apply the term epimerism to express the relation between two aldoses which differ only in the configuration of the carbon atom adjacent to the aldehyde grouping.

[81] E. Votoček and C. Krauz, *Ber.*, 1911, **44**, 3287; *A.*, 1912, i, 8.

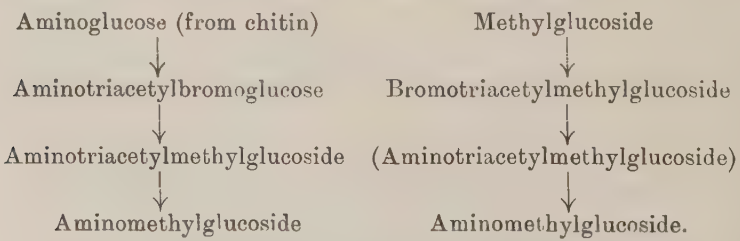
[82] E. Votoček, *ibid.*, 362; *A.*, i, 179.

[83] P. A. Levene and W. A. Jacobs, *ibid.*, 1910, **43**, 3141; *A.*, i, 14.



hence the formula for the corresponding aldehyde, *d*-altrose. The epimeric hexose, *d*-allose, is obtained from the more soluble *d*-allonic acid, which should yield *allo*-mucic acid on oxidation, but the latter relation has not yet been verified by experiment. The synthesis of homologous aldoses from dextrose has been carried as far as glucodecose,[84] but there is nothing sufficiently remarkable in this sugar or its relatives to warrant more than mention.

A new line of research in this group has been opened by the study of aminomethylglucosides; as yet the work has not proceeded far, but the preliminary results indicate that it will be of interest. An aminomethylglucoside has been prepared by two different processes,[85] which are indicated by the following schemes:



The products of these two methods are different, for that given

[84] L. H. Philippe, *Compt. rend.*, 1910, **151**, 986, 1366; 1911, **152**, 1774; *A.*, i, 12, 112, 605.

[85] E. Fischer and K. Zach, *Ber.*, 1911, **44**, 132; *A.*, i, 117; J. C. Irvine, D. McNicoll, and A. Hynd, *Trans.*, 1911, **99**, 250.

by the former may be hydrolysed to the ordinary glucosamine which served as the starting material, whilst that given by the latter yields a different aminoglucose. The precise relation between these compounds remains to be discovered.

A new disaccharide, vicianose,[86] has been obtained from the glucoside vicianin which occurs in the vetch. Since oxidation and subsequent hydrolysis of the product yields gluconic acid and arabinose, the constitution of this sugar is probably:

$$O\begin{cases}CH\cdot[CH\cdot OH]_2\cdot CH_2\cdot OH\\ |\\ CH\cdot O\cdot CH_2\cdot[CH\cdot OH]_4\cdot CHO\end{cases}$$

The production of synthetic glucosides has continued. In these syntheses advantage is taken of the reactivity of the halogen in substances such as acetobromoglucose and acetochloroglucose. To obtain the glucosides of complex alcohols such as geraniol, *cyclo*hexanol, and similar substances, it is sufficient to treat[87] these in ethereal solution with the halogen derivative and silver oxide. The same method has led to the production of glucosides derived from the phenolcarboxylic acids,[88] the methyl esters being employed to mask the undesirable effect of the carboxyl group.

The glucoside solanine, $(C_{27}H_{46}O_9N)_2,H_2O$, which is contained in *Solanum sodomaeum*, has been submitted to a thorough investigation.[89] When treated with hydrolytic agents it furnishes galactose, a methylpentose, and the base solanidine, $C_{18}H_{31}ON$. Little is yet known of the latter substance except that it contains hydroxyl and the imino-group.

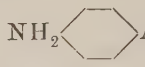
Organic Compounds of Arsenic.

Organic compounds of arsenic, although they have been known from the middle of the eighteenth century,[90] did not attract much attention until about four years ago; since that time, chiefly through the circumstance that they are of extreme value in the treatment of diseases of protozoal origin, their study has been eagerly prosecuted.

The new development of the chemistry of arsenic had its origin in the discovery of Ehrlich and Bertheim[91] that the compound, obtained in 1863 by Béchamp[92] by heating together aniline and

[86] G. Bertrand and G. Weisweiller, *Compt. rend.*, 1910, **151**, 884; *A.*, i, 15.
[87] E. Fischer and B. Helferich, *Annalen*, 1911, **383**, 69; *A.*, i, 802.
[88] F. Mauthner, *J. pr. Chem.*, 1911, [ii], **83**, 556; *A.*, i, 647.
[89] G. Oddo and M. Cesaris, *Gazzetta*, 1911, **41**, 490, 534; *A.*, i, 670, 671.
[90] Louis Claude Cadet-de-Gassicourt, *Mem. Math. Phys. Acad. Roy.*, 1760, **3**, 635.
[91] P. Ehrlich and A. Bertheim, *Ber.*, 1907, **40**, 3292; *A.*, 1907, i, 812.
[92] M. A. Béchamp, *Compt. rend.*, 1863, **56**, 1173.

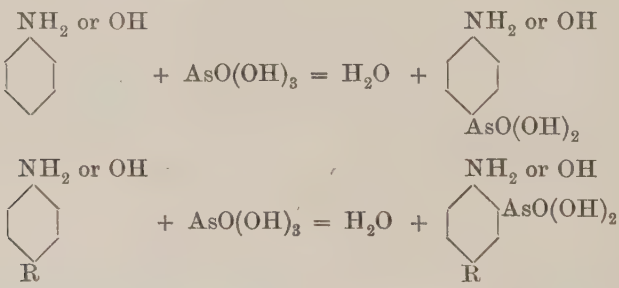
arsenic acid and considered by him to be the anilide of arsenic acid, $C_6H_5{\cdot}NH{\cdot}AsO(OH)_2$, was in reality *p*-aminophenylarsinic acid of the structure:



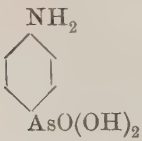
The proof that this compound, the sodium salt of which had come into extensive therapeutic use under the name "atoxyl," was not a chemically indifferent anilide, but a stable amino-derivative capable of taking part in the many reactions associated with such compounds, opened a wide field for investigation.

As a result of the work of the last four years an immense number of compounds containing arsenic similarly attached to various aromatic residues has been prepared, these again serving as starting points for the elaboration of new substances varying enormously in toxicity and applicability as curative agents.

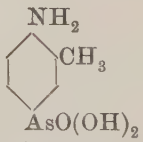
Arsinic acids can be obtained from many aromatic amines and phenols having an unsubstituted para- or ortho-position by heating them with arsenic acid to a temperature approaching 200°, when water is eliminated, thus:



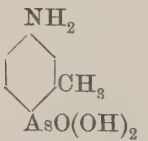
Arylamines with a free para-position relative to the amino-group yield *p*-arsinic acids; thus,[93] aniline, *o*-toluidine, *m*-toluidine, *o*-chloroaniline, *p*-xylidine, α-naphthylamine, and phenol yield respectively:



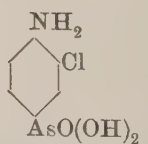
p-Aminophenylarsinic acid. (Arsanilic acid.)



2-Aminotolyl-5-arsinic acid.

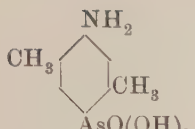


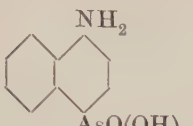
5-Aminotolyl-2-arsinic acid.

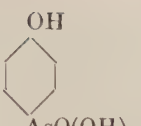


3-Chloro-4-aminophenylarsinic acid.

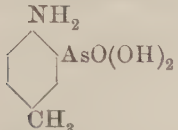
[93] P. Ehrlich and A. Bertheim, *Ber.*, 1907, **40**, 3292; *A.*, 1907, i, 812; O. Adler and R. Adler, *ibid.*, 1908, **41**, 931; *A.*, 1908, i, 492; L. Benda and R. Kahn, *ibid.*, 1672; *A.*, 1908, i, 591; D.R.-P. 205616; *A.*, 1909, i, 279.

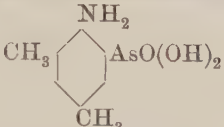

5-Amino-*p*-xylene-2-arsinic acid.

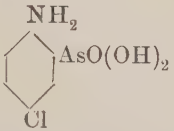

4-Aminonaphthyl-arsinic acid.


p-Hydroxyphenyl-arsinic acid.

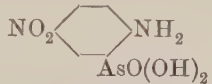
Arylamines substituted in the para-position [94] relatively to the amino-group react similarly with arsenic acid, yielding aminoaryl-*o*-arsinic acids, but the yields are generally poor; for example, *p*-toluidine, *m*-xylidine, and *p*-chloroaniline yield:


4-Aminotolyl-3-arsinic acid.


4-Amino-*m*-xylene-5-arsinic acid.


5-Chloro-2-aminophenyl-arsinic acid.

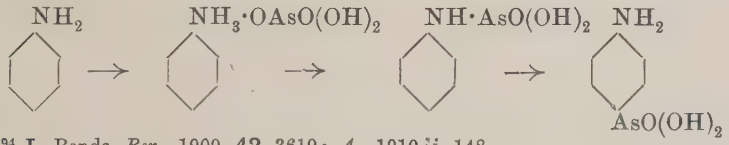
An important exception, however, is found in the case of *p*-nitro-aniline, which is relatively easily attacked,[95] giving:


5-Nitro-2-aminophenylarsinic acid.

Arsenic acid frequently oxidises arylamines, as in the well known preparation of magenta; the most advantageous methods of procedure have therefore been carefully worked out.

The action between an arylamine and arsenic acid at 170—200° does not stop at the formation of a monoarylarsinic acid, but proceeds if sufficient arylamine is present, and the heating is protracted to the formation of a diarylarsinic acid,[96] $R_2As{\cdot}O{\cdot}OH$; thus aniline yields di-*p*-aminophenylarsinic acid, and *o*-toluidine, di-2-aminotolyl-5-arsinic acid.[97]

In this process, as in the alkylation, nitration, sulphonation, and halogenation of arylamines, addition of the substituting agent to the amino-group of the base undoubtedly first takes place, followed probably by elimination of water and intramolecular rearrangement; for example, in the interaction of arsenic acid and aniline we have:



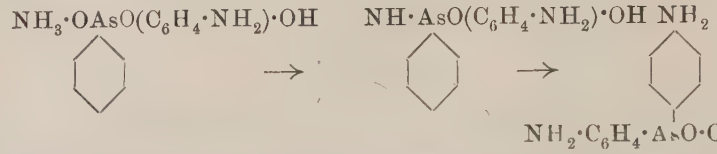
[94] L. Benda, *Ber.*, 1909, **42**, 3619; *A.*, 1910, i, 148.

[95] L. Benda, *ibid.*, 1911, **44**, 3293; *A.*, 1912, i, 61.

[96] L. Benda, *ibid.*, 1908, **41**, 2367; *A.*, 1908, i, 747.

[97] See also F. L. Pyman and W. C. Reynolds, *Trans.*, 1908, **93**, 1180; L. Benda and R. Kahn, *Ber.*, 1908, **41**, 1672; *A.*, 1908, i, 591.

the further interaction of the arsinic acid and aniline being represented as:



Mixed diaminodiarylarsinic acids can be similarly prepared by heating an arsinic acid with a base containing a different aryl group.

The aminic hydrogen atom of arsinic acids can be replaced by alkyl or similar groups; for example, *p*-dimethylaminophenylarsinic acid, $NMe_2 \cdot C_6H_4 \cdot AsO(OH)_2$,[98] is obtained by the action of methyl sulphate on an alkaline solution of sodium *p*-aminophenylarsinate, whilst phenylglycine-*p*-arsinic acid,[99]

$$CO_2H \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot AsO(OH)_2,$$

is obtained by heating for some hours a solution of the latter salt with chloroacetic acid or by hydrolysing with alkali the nitrile, $CN \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot AsO(OH)_2$, produced by heating together in aqueous solution *p*-aminophenylarsinic acid, sodium cyanide, and formaldehyde. Phenylglycine-*p*-arsinic acid is of therapeutic value on account of its slight toxicity.

The aminic hydrogen atom can also be easily replaced by acyl groups[1] by ordinary methods; *p*-acetylaminophenylarsinic acid (arsacetin), obtained by allowing acetic anhydride to react with *p*-aminophenylarsinic acid or its sodium salt, and the oxalyl derivative, $CO_2H \cdot CO \cdot NH \cdot C_6H_4 \cdot AsO(OH)_2$, prepared by heating either of the last two substances with oxalic acid,[2] are of considerable importance.

The introduction of an acetyl group diminishes the toxic effect of the compound, whilst the presence of the oxalyl group confers greater stability, and allows the compound to be used for the preparation of various substitution derivatives.

Carbamides[3] of the general formula

$$NRR' \cdot CO \cdot NH \cdot C_6H_4 \cdot AsO(OH)_2,$$

where R and R′ may be either hydrogen or an alkyl or aryl group, are yielded by the interaction of *p*-aminophenylarsinic acid with cyanic acid or its esters. Other arylarsinic acids behave similarly.

[98] A. Michaelis, *Ber.*, 1908, **41**, 1514; *A.*, 1908, i, 590.

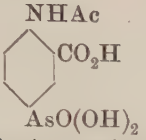
[99] D.R.-P. 204664; *A.*, 1909, i, 280.

[1] P. Ehrlich and A. Bertheim, *Ber.*, 1907, **40**, 3296; *A.*, 1907, i, 812; D.R.-P 191548; *A.*, 1908, i, 591.

[2] A. Bertheim, *Ber.*, 1911, **44**, 3092; *A.*, i, 1055; D.R.-P. 231969; *A.*, i, 594.

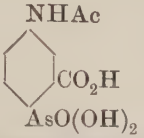
[3] D.R.-P. 213155; *A.*, 1910, i, 148.

Acyl derivatives of the methyl homologues of the arylarsinic acids are easily oxidised by potassium permanganate in alkaline solution into the corresponding carboxyarsinic acids; for example, 2-acetylaminotolyl-5-arsinic acid and 3-acetylaminotolyl-6-arsinic acid yield:



4-Acetylamino-3-carboxyphenylarsinic acid.

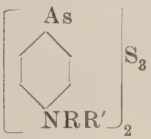
and



4-Acetylamino-2-carboxyphenylarsinic acid.

respectively.[4]

By the action of hydrogen sulphide on the arsinic acids and their derivatives, the oxygen and hydroxyl groups are replaced by sulphur, with the formation of compounds of the general formulæ[5]:



and

All the amino- and diamino-arsinic acids are easily diazotised,[6] the diazonium salts produced being able to take part in all the reactions characteristic of these compounds; for example, when heated with water they yield the corresponding hydroxy-compounds; thus, *p*-hydroxyphenylarsinic acid, $HO{\cdot}C_6H_4{\cdot}AsO(OH)_2$, 2-hydroxytolyl-5-arsinic acid, $HO{\cdot}C_7H_6{\cdot}AsO(OH)_2$, 4-hydroxy-3-carboxyphenylarsinic acid (salicylarsinic acid), and 4:4′-dihydroxydiphenylarsinic acid $(HO{\cdot}C_6H_4)_2AsO{\cdot}OH$, are obtained from *p*-aminophenylarsinic acid, 2-aminotolyl-5-arsinic acid, 4-amino-3-carboxyphenylarsinic acid, and 4:4′-diaminodiphenylarsinic acid respectively.

The diazotised arsinic acids couple with various amines and phenols.

In all the arsinic acids and their derivatives the arsenic is in the quinquevalent condition. As, however, compounds in which it is in the more active tervalent condition have an enormously greater toxic effect on trypanosomes, many reduction products of the former have been prepared of the types R·AsO,

$$R{\cdot}AsOH{\cdot}AsOH{\cdot}R,$$

[4] O. Adler and R. Adler, *Ber.*, 1908, **41**, 931; *A.*, 1908, i, 492; R. Kahn and L. Benda, *ibid.*, 3859; *A.*, 1909, i, 75.

[5] D.R.-P. 205617.

[6] R. Kahn and L. Benda, *Ber.*, 1908, **41**, 3859; *A.*, 1909, i, 75; O. Adler and R. Adler, *ibid.*, 931; *A.*, 1908, i, 492; L. Benda, *ibid.*, 2367; *A.*, 1908, i, 742; M. Barrowcliff, F. L. Pyman, and F. G. P. Remfry, *Trans.*, 1908, **93**, 1893.

and R·As:AsR. Reduction of an arsinic acid to one or other of these stages can be effected by employing a reducing agent of appropriate strength.

Among those[7] which have been often used in the reduction of aminoarylarsinic compounds are sodium amalgam in methyl alcohol, stannous chloride in concentrated hydrochloric acid, sometimes with a little hydriodic acid as catalyst, sulphur dioxide in the presence of a little hydriodic acid as catalyst, and, lastly, sodium hyposulphite.

Reduction of an arsinic acid to an arseno-compound can be carried out in one operation, or an arsenious oxide may be isolated as an intermediate product. Direct reduction appears simple, but at times yields a less pure product than when it is carried out in two stages. Speaking generally, reducing agents act less readily on compounds containing quinquevalent than on compounds containing tervalent arsenic.

In preparing the arylarsenious oxides, sulphur dioxide in presence of a little hydriodic acid is very advantageously employed. Sulphur dioxide itself acts very slowly on arsinic acids, whilst the action of hydriodic acid is reversible; thus, for example:

$$NH_2\cdot C_6H_4\cdot AsO(OH)_2 + 2HI \rightleftharpoons NH_2\cdot C_6H_4\cdot AsO + 2H_2O + I_2.$$

The arylarsinic acids are therefore best reduced to the arylarsenious oxides by dissolving their sodium salts in water, adding a little potassium iodide, and passing sulphur dioxide for some hours. On adding ammonia, the arsenious oxides separate, usually as white, crystalline solids.

p-Aminophenylarsenious oxide, $NH_2\cdot C_6H_4\cdot AsO$, *p*-hydroxyphenylarsenious oxide,[8] $HO\cdot C_6H_4\cdot AsO$, 2-aminotolyl-5-arsenious oxide,[9] $NH_2\cdot C_7H_6\cdot AsO$, and 3-amino-4-hydroxyphenylarsenious oxide,[10] $NH_2\cdot C_6H_3(OH)\cdot AsO$, are thus obtained from the corresponding arsinic acids.

In *p*-aminophenylarsenious oxide the linking between arsenic and carbon is very much looser than in arsinic acids, and when the oxide is heated with dilute hydrochloric acid, it is converted into arsenious oxide and triaminotriphenylarsine[11]:

$$3NH_2\cdot C_6H_4\cdot AsO = (NH_2\cdot C_6H_4)_3As + As_2O_3.$$

This latter forms a well crystallised triacetyl derivative, which, when dissolved in dilute acetic acid containing excess of sodium acetate, is converted by the action of iodine into triacetylamino-

[7] P. Ehrlich and A. Bertheim, *Ber.*, 1910, **43**, 917; *A.*, 1910, i, 451; *ibid.*, 1911, **44**, 1260; *A.*, i, 593.

[8] D.R.-P. 213594; *A.*, 1910, i, 148.

[9] D.R.-P. 212205; *A.*, 1910, i, 84.

[10] D.R.-P. 235391; *A.*, i, 1055.

[11] P. Ehrlich and A. Bertheim, *Ber.*, 1910, **43**, 923; *A.*, 1910, i, 451.

triphenylarsinic oxide, $(CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4)_3AsO$, a compound previously obtained by acetylating triaminotriphenylarsine oxide,[12] $(NH_2{\cdot}C_6H_4)_3AsO$, obtained by the prolonged interaction of arsenious chloride and aniline in boiling toluene, and subsequent decomposition of the condensation product by boiling aqueous sodium carbonate.

p-Aminophenylarsenious oxide dissolved in sodium hydroxide reacts with chloroacetic acid,[13] forming *p*-aminophenylarsenoacetic acid, $NH_2{\cdot}C_6H_4{\cdot}As(OH)O{\cdot}CH_2{\cdot}CO_2H$. The halogen alkyls react similarly, giving a notable extension of G. Meyer's method of preparing primary arsinic acids from sodium arsenate and halogen alkyl.

The aminoarylarsenious oxides are converted by the action of strong solutions of the halogen hydrides into salts of the corresponding arsine dihalides; for example, *p*-aminophenylarsine oxide yields with concentrated hydrochloric acid the hydrochloride of *p*-aminophenylarsine dichloride, $NH_2{\cdot}C_6H_4{\cdot}AsCl_2,HCl$, and corresponding compounds with hydrobromic and hydriodic acids.[14]

When *p*-aminophenylarsinic acid is similarly heated with fuming hydriodic acid the hydriodide of *p*-aminoarsine tetraiodide, $NH_2{\cdot}C_6H_4{\cdot}AsI_4,HI$, is formed.[15]

4 : 4′-Diaminodihydroxyarsenobenzene,[16] the compound intermediate between *p*-aminoarsenious oxide and 4 : 4′-diaminoarsenobenzene:

$$NH_2{\cdot}C_6H_4{\cdot}AsO \longrightarrow NH_2{\cdot}C_6H_4{\cdot}As(OH){\cdot}As(OH){\cdot}C_6H_4{\cdot}NH_2 \longrightarrow NH_2{\cdot}C_6H_4{\cdot}As{:}As{\cdot}C_6H_4{\cdot}NH_2,$$

has been obtained by reducing the former, dissolved in methyl alcohol, with sodium amalgam. Sodium hyposulphite[17] is an especially useful reducing agent for converting the arsinic acids or arsenious oxides into arseno-compounds. It is generally employed in presence of alkali and magnesium chloride, the latter being found to diminish the formation of by-products in such reductions.

The arsinic acid is generally digested with a slightly warmed solution of sodium hyposulphite containing sodium hydroxide and magnesium chloride. Sodium *p*-aminophenylarsinate when thus reduced yields 4 : 4′-diaminoarsenobenzene, and sodium *p*-hydroxyphenylarsinate yields 4 : 4′-dihydroxyarsenobenzene[18]:

[12] G. T. Morgan and Miss F. M. G. Micklethwait, *Trans.*, 1909, **95**, 1473.

[13] W. M. Dehn and S. J. McGrath, *J. Amer. Chem. Soc.*, 1906, **28**, 347; *A.*, 1906, i, 341.

[14] A. Bertheim, *Ber.*, 1911, **44**, 1070; *A.*, i, 593.

[15] A. Patta and P. Caccia, *Boll. Soc. Med. Chirurg. Pavia*, 1911; *A.*, i, 1554.

[16] D.R.-P. 206057; *A.*, 1909, i, 347.

[17] P. Ehrlich and A. Bertheim, *Ber.*, 1911, **44**, 1265; *A.*, i, 593.

[18] D.R.-P. 206456; *A*, 1909, i, 347; *ibid.*, 213594; *A.*, 1910, i, 148.

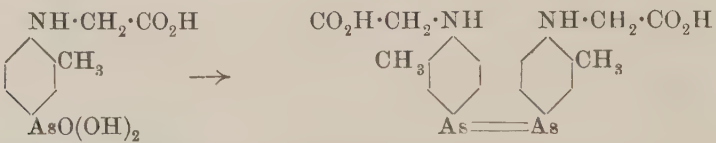
Arseno-*o*-cresol, $As_2(C_6H_3Me{\cdot}OH)_2$, is similarly prepared from 2-hydroxytolyl-5-arsinic acid, whilst tetrachloro-, tetrabromo-, and tetraiodo-arsenophenols are obtained from the corresponding halogenated derivatives of *p*-hydroxyphenylarsinic acid.[19]

All amino- or hydroxy-phenylarsinic acids and their substitution products yield their corresponding arseno-compounds.

These arseno-compounds can neither be distilled nor crystallised, and many possess colloidal properties. Even in the solid state they oxidise in the air, and to be kept unchanged must be sealed in tubes exhausted or filled with some indifferent gas.

Arsenophenylglycine,[20] $As_2(C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO_2H)_2$, prepared by reducing phenylglycinearsinic acid, $CO_2H{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}AsO(OH)_2$, on account of its low toxicity has been extensively employed in medicine.[21]

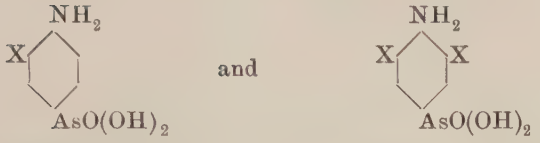
p-Arseno-*o*-tolylglycine [22] is similarly obtained from *o*-tolylglycine-5-arsinic acid:



Phenylglycol-*p*-arsinic acid, $CO_2H{\cdot}CH_2{\cdot}O{\cdot}C_6H_4{\cdot}AsO(OH)_2$, prepared by heating *p*-hydroxyphenylarsinic acid dissolved in aqueous alkali with chloroacetic acid, yields, when thus reduced, arsenomandelic acid,[23] $As_2(C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CO_2H)_2$, a compound possessing powerful trypanocidal properties.

The arsenic acid residue, $\cdot AsO(OH)_2$, which is so firmly attached to the ring in arsinic acids that it is not affected in most reactions in which these compounds take part, is easily removed by halogens; thus an aqueous solution of *p*-aminophenylarsinic acid gives an almost quantitative yield of *s*-tribromoaniline when mixed with bromine water. By very careful halogenation, however, Bertheim [24] has succeeded in preparing mono- and di-halogen aminoarylarsinic acids of the types:

[19] D.R.-P. 235430; *A.*, i, 1055.
[20] D.R.-P. 206057; *A.*, 1909, i, 347.
[21] P. Ehrlich, *Ber.*, 1909, **42**, 36.
[22] D.R.-P. 212205; *A.*, 1910, i, 84.
[23] D.R.-P. 216270; *A.*, 1910, i, 452.
[24] A. Bertheim, *Ber.*, 1910, **43**, 529; *A.*, 1910, i, 346.



By careful treatment the hydroxyarylarsinic acids can be similarly substituted; for example, sodium *p*-hydroxyphenylarsinate gives with sodium hypochlorite or hypobromite the dihalogenated acid.[25]

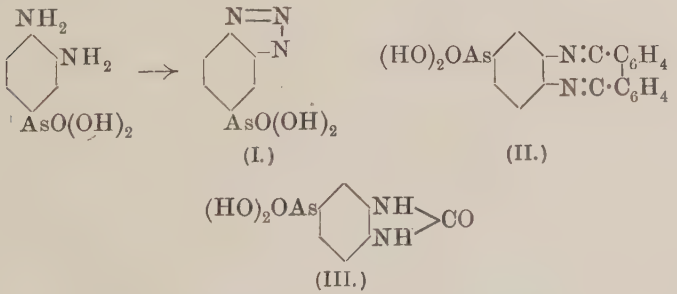
The nitration of the arsinic acids has led to results of great importance.

Neither *p*-aminophenylarsinic acid nor its acetyl derivative can be nitrated without considerable decomposition. One nitro-group is, however, easily introduced if oxalyl-*p*-aminophenylarsinic acid, $CO_2H{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}AsO(OH)_2$, is cautiously nitrated with a mixture of nitric and sulphuric acids.[26] On hydrolysis, 3-nitro-4-aminophenylarsinic acid, $NH_2{\cdot}C_6H_3(NO_2){\cdot}AsO(OH)_2$, is obtained.

The urethane, $CO_2Et{\cdot}NH{\cdot}C_6H_4{\cdot}AsO(OH)_2$, obtained by the action of ethyl chlorocarbonate on *p*-aminophenylarsinic acid, can be used in place of the oxalyl derivative.[27]

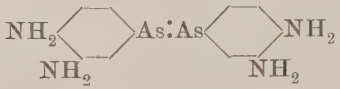
3-Nitro-4-aminophenylarsinic acid has also been obtained by heating together arsenic acid and *o*-nitroaniline.[28]

When the sodium salt of 3-nitro-4-aminophenylarsinic acid is cautiously reduced by the calculated amount of sodium hyposulphite, 3 : 4-diaminophenylarsinic acid, $C_6H_3(NH_2)_2{\cdot}AsO(OH)_2$, is produced.[29] This behaves as a typical orthodiamine, and forms an azimino-compound (I) with nitrous acid, a quinoxaline (II) with phenanthraquinone, and a cyclic carbamide (III) with carbonyl chloride, thus:



[25] D.R.-P. 235430; *A.*, i, 1055.
[26] A. Bertheim, *Ber.*, 1911, **44**, 3092; *A.*, i, 1155; D.R.-P. 231969.
[27] D.R.-P. 232879.
[28] E. Mameli, *Boll. Chim. Farm.*, 1909, **48**, 682; *A.*, 1909, i, 980.
[29] A. Bertheim, *Ber.*, 1911, **44**, 3092; *A.*, i, 1055.

It is converted by energetic reduction into tetra-aminoarsenobenzene:

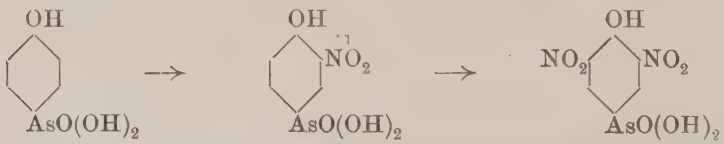


It is noteworthy [30] that when 3-nitro-4-aminophenylarsinic acid is heated to about 80° with a solution of potassium hydroxide, the amino-group is replaced by hydroxyl, ammonia being evolved, and 3-nitro-4-hydroxyphenylarsinic acid produced:

5-Nitro-2-aminophenylarsinic acid [31] and 3-nitro-2-aminotolyl-5-arsinic acid behave similarly.

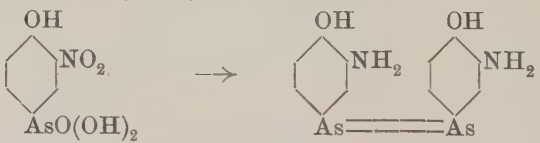
The therapeutically active hydroxyarylarsinic acids obtained either directly from the phenols or indirectly [32] through the amino-arylarsinic acids can be nitrated more easily than the corresponding amino-compounds.

Direct nitration of *p*-hydroxyphenylarsinic acid by a mixture of nitric and sulphuric acids yields either the mono- or di-nitro-compound,[33] according to the amount of nitric acid used and the temperature at which the operation is conducted:



When reduced by means of gentle reducing agents these yield the corresponding aminohydroxyphenylarsinic acids, whilst more vigorous reduction leads to the formation of arseno-derivatives.

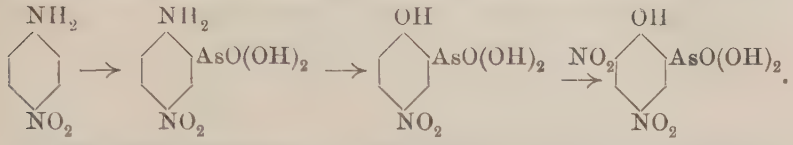
When [34] 3-nitro-4-hydroxyphenylarsinic acid is reduced by digesting its sodium salt dissolved in sodium hydroxide with excess of sodium hyposulphite in the presence of magnesium chloride, it yields 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene:



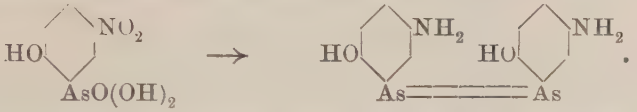
[30] D.R.-P. 235141; *A.*, i, 1056.
[31] L. Benda, *Ber.*, 1911, **44**, 3293; *A.*, 1912, i, 61.
[32] L. Benda, *ibid.*, 3449; *A.*, 1912, i, 64.
[33] L. Benda and A. Bertheim, *ibid.*, 3445; *A.*, 1912, 63.
[34] D.R.-P. 224953; *A.*, 1910, i, 803.

The dihydrochloride of this base is the much-discussed compound "salvarsan."

5-Nitro-2-hydroxyphenylarsinic acid, prepared from the amino-acid obtained from *p*-nitroaniline, behaves in a similar way to its isomeride.[35] When nitrated it yields a dinitro-derivative:

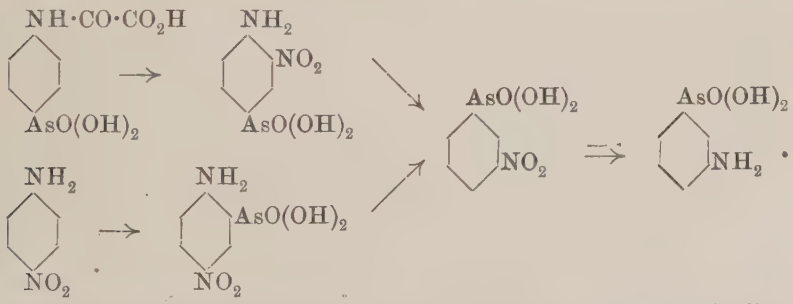


and when strongly reduced, as, for example, by sodium hyposulphite, 5 : 5′-diamino-2 : 2′-dihydroxyarsenobenzene is formed:



The dihydrochloride of this base is isomeric with salvarsan.

Different nitroaminophenylarsinic acids, in which the nitro-group is in the meta-position relatively to the arsinic acid residue, are furnished by the nitration of oxalyl-*p*-aminoarsinic acid, and also from *p*-nitroaniline; from either of these, by diazotisation and replacement of the diazonium group by hydrogen, *m*-nitrophenylarsinic acid can be obtained. This when dissolved in methyl alcohol and reduced by sodium amalgam gives *m*-aminophenylarsinic acid[36]:

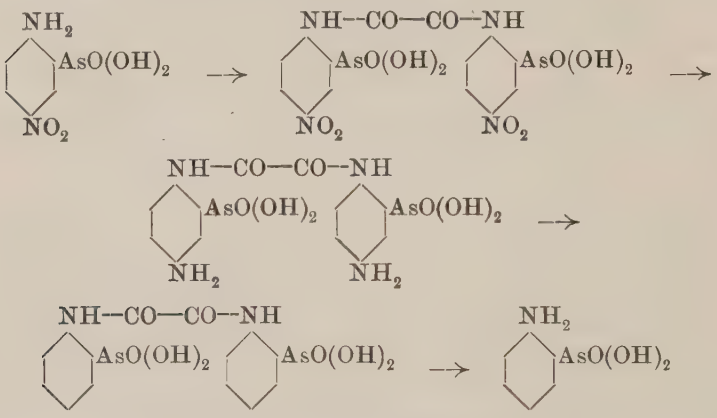


5-Nitro-2-aminophenylarsinic acid when reduced in alkaline solution by ferrous oxide yields 2 : 5-diaminophenylarsinic acid[37]; this, however, by diazotisation and replacement of the diazonium group by hydrogen yields only the *m*-aminophenylarsinic acid, and not, as might have been expected, the isomeric ortho-compound.

Further, 5-nitro-2-acetylaminophenylarsinic acid is so unstable that it cannot be reduced without hydrolysis occurring; the oxalyl

[35] L. Benda, *Ber.*, 1911, **44**, 3293; *A.*, 1912, i, 61.
[36] A. Bertheim and L. Benda, *ibid.*, 3297; *A.*, 1912, i, 62.
[37] L. Benda, *ibid.*, 3300; *A.*, 1912, i, 62.

derivative, however, obtained by heating the sodium salt of the acid with oxalic acid to 175°, is more stable, and can be reduced to the corresponding amino-compound by means of iron powder and dilute acetic acid. This on diazotisation and replacement of the diazonium group by hydrogen yields an oxalyl derivative, from which *o*-aminophenylarsinic acid is obtained by hydrolysis [38]:



The three possible aminophenylarsinic acids being now known, it was possible to identify the amino-acid [39] yielded on reduction of the acid obtained in the direct nitration of phenylarsinic acid.[40] This proved to be identical with *m*-aminophenylarsinic acid; consequently the nitro-acid has the meta-configuration, and the arsinic acid residue belongs to the group of substituents, including the analogous groups NO_2 and SO_3H, which direct other entering groups into the meta-position.

3-Nitro-4-aminophenylarsinic acid on diazotisation yields a diazonium salt, which when heated for some time to 18° in dilute acid solution containing an excess of sodium acetate exchanges its nitro-group for hydroxyl, giving a new diazonium salt, and this in alkaline solution couples with β-naphthol. The colouring matter produced yields on reduction either 4-amino-3-hydroxyphenylarsinic acid or 4 : 4′-diamino-3 : 3′-dihydroxyarsenobenzene, according to conditions.

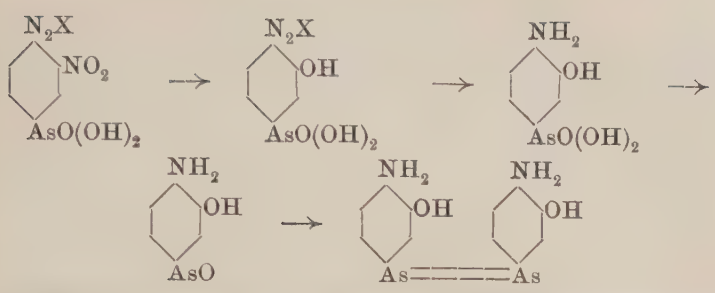
The former of these when reduced by sulphurous acid and a little hydriodic acid yields 4-amino-3-hydroxyphenylarsenious oxide, which itself can be further reduced to the arseno-compound [41]:

[38] L. Benda, *Ber.*, 1911, **44**, 3304; *A.*, 1912, i, 63.

[39] D.R.-P. 206344; *A.*, 1909, i, 448.

[40] A. Michaelis, *Ber.*, 1894, **27**, 263; *A.*, 1894, i, 187; *Annalen*, 1902, **320**, 294.

[41] L. Benda, *ibid.*, 1911, **44**, 3578.



The dihydrochloride of 4 : 4′-diamino-3 : 3′-dihydroxyarsenobenzene is a third isomeride of salvarsan.

Organic Compounds of Antimony.

An interesting point has arisen in connexion with the preparation of phenylstibine dichloride, $C_6H_5 \cdot SbCl_2$. This was first obtained by Hasenbäumer [42] by heating triphenylstibine with antimony trichloride in xylene at 240°. In a recent communication Michaelis and Günther [43] state that they always obtain in this reaction diphenylstibine chloride, $(C_6H_5)_2SbCl$. Both these observations prove to be correct, the experiments of Morgan and Miss Micklethwait [44] showing that the action is a balanced one in the sense indicated by the equations:

$$2(C_6H_5)_3Sb + SbCl_3 \rightleftharpoons 3(C_6H_5)_2SbCl$$
$$(C_6H_5)_2SbCl + SbCl_3 \rightleftharpoons 2C_6H_5 \cdot SbCl_2$$

Diphenylstibine chloride when digested with aqueous sodium carbonate yields diphenylstibine oxide, which when acted on by hydrogen sulphide gives the corresponding sulphide. It also combines with chlorine, forming diphenylstibine trichloride, which is decomposed by hot alkalis, giving a solution from which dilute sulphuric acid precipitates diphenylstibinic acid:

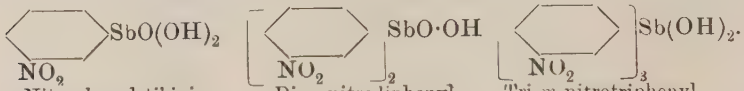
$$(C_6H_5)_2SbCl \begin{cases} \nearrow [(C_6H_5)_2Sb]_2O \longrightarrow [(C_6H_5)_2Sb]_2S \\ \searrow (C_6H_5)_2SbCl_3 \longrightarrow (C_6H_5)_2SbO \cdot OH \end{cases}$$

When treated with alcoholic silver nitrate, triphenylstibine dichloride is converted into triphenylstibine nitrate.[45] This, however, is not stable, and is converted by partial hydrolysis into triphenylstibine hydroxynitrate, which may be recrystallised from hot water without further change:

$$(C_6H_5)_3SbCl_2 \longrightarrow (C_6H_5)_3Sb(NO_3)_2 \longrightarrow (C_6H_5)_3Sb(OH) \cdot NO_3.$$

[42] J. Hasenbäumer, *Ber.*, 1898, **31**, 2910 ; *A.*, 1899, i, 209.
[43] A. Michaelis and A. Günther, *ibid.*, 1911, **44**, 2316 ; *A.*, i, 1056.
[44] G. T. Morgan and Miss F. M. G. Micklethwait, *Trans.*, 1911, **99**, 2288.
[45] G. T. Morgan and Miss F. M. G. Micklethwait, *ibid.*, 1910, **97**, 35.

Morgan and Miss Micklethwait[46] also find that phenylstibinic acid, diphenylstibinic acid, and triphenylstibine hydroxynitrate, when nitrated with a mixture of concentrated nitric and sulphuric acids, yield nitro-derivatives:



m-Nitrophenylstibinic acid.

Di-*m*-nitrodiphenylstibinic acid.

Tri-*m*-nitrotriphenylstibinic acid.[47]

one nitro-group entering each benzene nucleus in a meta-position with respect to the antimonic substituent.

The presence of quinquevalent antimony in the benzene ring thus influences the introduction of a second group in accordance with the meta-law of substitution.

By reducing tri-*m*-nitrotriphenylstibinic acid, dissolved in boiling alcohol, by means of zinc dust and ammonium chloride, tri-*m*-aminotriphenylstibine, $Sb(C_6H_4{\cdot}NH_2)_3$, has been obtained.[46] It forms a crystalline hydrochloride, $Sb(C_6H_4{\cdot}NH_2,HCl)_3$.

Organic Compounds of Sulphur.

The readiness with which sulphur passes from the lower to the higher states of valency and the reactivity with which it is endowed when in the bi- and quadri-valent conditions give rise to many reactions of peculiar interest in carbon compounds which contain this element. Although most of the chief types of these substances were known before 1870, very little attention was given to the study of their reactivity during the development of modern organic chemistry. It seems, however, from the continually increasing number of chemists working with these compounds that interest in this field of work is being somewhat revived, and there is no doubt that those who take up the investigation will find many problems of interest awaiting solution. Since it would be out of place here to discuss these questions, attention may be at once directed to the work of the past year. When sulphur in organic compounds is progressively saturated with oxygen, the stability of the complex continually rises until a maximum is reached in substances such as the sulphones, which contain this element in the sexavalent state. In the lower stages of oxidation the stability of the group is very much less, and it is not surprising that efforts to isolate the sulphoxylic acids, R·SOH, have not yet met with success. Hitherto the fleeting existence of these substances has been deduced, although not always with certainty, from the

[46] G. T. Morgan and Miss F. M. G. Micklethwait, *Trans.*, 1911, **99**, 2288.
[47] P. May, *ibid.*, 1910, **97**, 1958.

behaviour of certain unstable compounds of bi- and quadri-valent sulphur; but recently substances have been isolated which are evidently closely related to these acids. Hitherto the so-called perchloromethylmercaptan, $CCl_3 \cdot SCl$, which may be regarded as the chloride of the sulphoxylic acid, has been the only representative of its class; but it has been shown [48] that a new series of aromatic derivatives may be obtained by the interaction of chlorine and suitable disulphides; for example:

$$NO_2 \cdot C_6H_4 \cdot S \cdot S \cdot C_6H_4 \cdot NO_2 + Cl_2 = 2NO_2 \cdot C_6H_4 \cdot SCl.$$

As might be anticipated, the halogen in these substances may be easily replaced by other groups, and it seems within the bounds of probability that by choosing a suitable condition of the benzene nucleus a relatively stable sulphoxylic acid might be isolated from them.

Clear proof of the existence of the sulphoxylic acids has been obtained [49] from the hydrolysis of the disulphides with concentrated sulphuric acid. It has long been known that the mercaptans are converted by oxidation with this reagent into the disulphides. The first stage in this interaction is the oxidation of part of the mercaptan to the sulphoxylic acid:

$$ArSH + O = ArS \cdot OH,$$

the latter then reacting with excess of mercaptan, forming the disulphide:

$$ArS \cdot OH + ArSH \rightleftarrows ArS \cdot SAr + H_2O.$$

It is also made evident that this interaction is reversible, although in most cases the equilibrium is greatly in favour of the disulphide; but by removing the sulphoxylic acid the balance may be upset, and hydrolysis of the disulphide rendered complete. Removal of the sulphoxylic acid may be effected by raising the temperature of the solution or by adding some reactive aromatic compound to the mixture. In the former case the previously observed synthesis of *o*-thianthrens [50] or of their para-isomerides [51] is obtained by intermolecular condensation of the sulphoxylic acid:

$$C_6H_5 \begin{matrix} S \cdot OH \\ HO \cdot S \end{matrix} C_6H_5 = 2H_2O + C_6H_4 \begin{matrix} S \\ S \end{matrix} C_6H_4,$$

whilst in the latter case unsymmetrical monosulphides are formed:

$$ArS \cdot OH + HAr' = ArSAr' + H_2O.$$

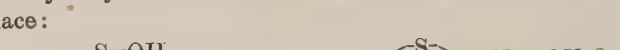
The last-named process may be applied to the synthesis of derivatives of thioxanthone.[52]

[48] T. Zincke, *Ber.*, 1911, **44**, 769; *A.*, i, 368.
[49] W. G. Prescott and S. Smiles, *Trans.*, 1911, **99**, 640.
[50] K. Fries and W. Volk, *Ber.*, 1909, **42**, 1170; *A.*, 1909, i, 406.
[51] T. P. Hilditch, *Trans.*, 1910, **97**, 2579.
[52] Miss E. G. Marsden and S. Smiles, *ibid.*, 1911, **99**, 1353.

A similar decomposition has been observed with the disulphoxides,[53] which yield the sulphinic and sulphoxylic acids as follows:

$$H_2O + ArSO{\cdot}SOAr = ArS{\cdot}OH + ArSO_2H.$$

If the hydrolytic mixture is heated, thianthren formation may take place:



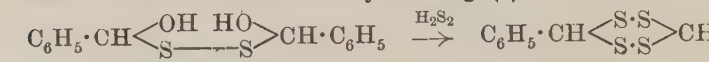
but if reactive substances such as phenetole are present, the sulphinic acid is converted into the sulphonium salt (1), whilst the sulphoxylic acid yields the monosulphide (2):

(1) $ArSO_2H + 2Ar'H = ArAr'_2S{\cdot}OH + H_2O.$

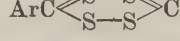
(2) $ArS{\cdot}OH + Ar'H = ArSAr' + H_2O.$

However, it may be observed that the course taken by these interactions depends to a great extent on the constitution of the reagents.

The study of the additive products formed by hydrogen persulphide with organic compounds has led to results of general interest. This reagent, like others which contain the sulphydric grouping, yields additive compounds with aromatic aldehydes,[54] that furnished with benzaldehyde being (I):



The isolation of these substances has led to a method of preparing the carbithionic acids. With excess of hydrogen persulphide in presence of a condensing agent, they are converted into resinous substances, which probably possess the structure (II) represented in the foregoing equation. The latter compounds are decomposed by potassium hydroxide, yielding the alkali salts of the carbithionic acids, $Ph{\cdot}CS_2H$; but even in the pure condition these acids are not very stable, being slowly oxidised by atmospheric oxygen to complex sulphides of the following type:



It is interesting to observe that with the accumulation of sulphur in the molecular complex an intense colour is developed, the phenyl derivative being violet and its esters deep red; but this is scarcely surprising in view of previous work[55] on the absorptive power exerted by this element in organic compounds. Camphorcarbithionic

[53] T. P. Hilditch, *Trans.*, 1910, **97**, 1091.

[54] I. Bloch, F. Höhn, and G. Bugge, *J. pr. Chem.*, 1910, [ii], **82**, 473; *A.*, i, 46; F. Höhn and G. Bugge, *ibid.*, 486; *A.*, i, 48; G. Bugge and I. Bloch, *ibid.*, 572; *A.*, i, 60.

[55] J. E. Purvis, *Proc. Camb. Phil. Soc.*, 1911, **16**, 155; *A.*, ii, 560; J. E. Purvis, H. O. Jones, and H. S. Tasker, *Ann. Report*, 1910, 250.

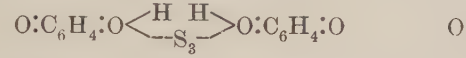
acid has been obtained[56] from the interaction of sodium camphor and carbon disulphide, but not much interest is attached to the substance; it decomposes with great ease into the components. Closer attention may be directed to the esters of the aliphatic carbothionic acids which have been thoroughly investigated.[57] Two methods of preparing these compounds have been discovered: either by treating an imino-ether with hydrogen sulphide (1), or from the interaction of magnesium alkyl halide and chlorothioformic ester (2):

(1) $RC(:NH)\cdot OR + H_2S = NH_3 + RCS\cdot OR$.

(2) $Cl\cdot CS\cdot OR + RMgX = MgXCl + R\cdot CS\cdot OR$.

The esters in question are slowly oxidised by atmospheric oxygen, and during the process a faint glow is emitted; the phenomenon has been termed "oxyluminescence."

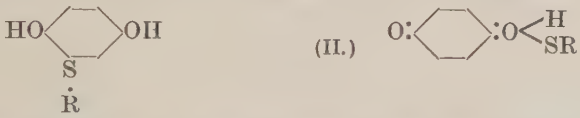
Further experiments with hydrogen persulphide have dealt with the additive compounds which it forms with quinones.[58] If the reagent is added to a solution of *p*-benzoquinone in an anhydrous solvent, a brilliantly blue substance is obtained, to which the oxonium structure (I) is assigned:



(I.) (II.)

Other intensely coloured substances of similar constitution are formed from quinones with hydrogen monosulphide or potassium hydrosulphide (II). The isolation of these substances is of some importance, since it indicates the course of interaction of mercaptans and similar substances with quinones. In such cases the nuclear derivative of the type (I) is obtained; but it now seems probable

(I.) (II.)



that these are formed in some manner from the oxonium additive products (II) which first occur.

Other researches have dealt with the conditions under which sulphur may become a component of the quinonoid arrangement. Observations on the simple thioquinones such as $S:C_6H_4:S$ are still wanting,[59] but the work of Kehrmann and others on the azo and

[56] L. A. Tschugaeff and G. Pigoulowsky, *Compt. rend.*, 1911, **153**, 388; *A.*, i, 797.

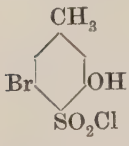
[57] M. Matsui, *Mem. Coll. Sci. Kyoto*, 1908, **1**, 285; *A.*, 1909, i, 463; M. Delépine, *Compt. rend.*, 1911, **153**, 279; *A.*, i, 768; *Bull. Soc. chim.*, 1911, [iv], **9**, 901; *A.*, i, 944.

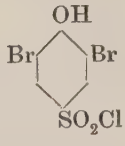
[58] M. M. Richter, *Ber.*, 1910, **43**, 3599; *A.*, i, 135.

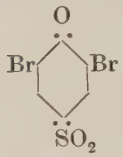
[59] See T. Zincke and W. Frohneberg, *ibid.*, 1909, **42**, 2721; *A.*, 1909, i, 643.

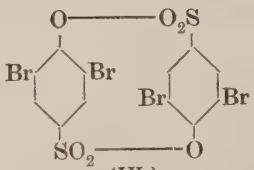
carbothionium salts has already shown that sulphur can assume this rôle when in the quadrivalent state. In substances of that type the quinonoid element forms part of a heterocyclic group, and some interest is therefore attached to the observation that it may exist in simpler quinonoid systems.

The simplest of these substances for which the quinonoid structure has been claimed are formed by eliminating hydrogen chloride from the chlorides of aromatic hydroxysulphonic acids; for example, both the ortho-[60] and para-[61]derivatives (I and II) yield

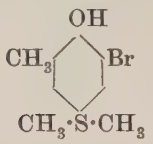

(I.)

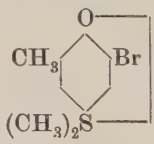

(II.)

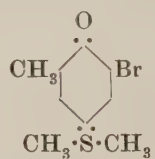

(III.)


(IV.)

bright yellow solutions when treated with sodium acetate in ether, but on attempting to isolate the products, colourless polymerides are obtained. In some cases (for example, III) these react with alcohol or aniline, yielding the ester or anilide of the sulphonic acid; but as a rule they are indifferent, and it must be admitted that what little evidence there is favours the intermolecular anhydride structure (IV), although it is probable that in the yellow solutions they exist as the true quinones. Similar experiments have dealt[62] with substances containing quadrivalent sulphur. When the sulphonium iodide (I) is treated with silver oxide a neutral substance is formed, which may be regarded either as the anhydride (II) or the sulphonium-quinone (III):


(I.)


(II.)


(III.)

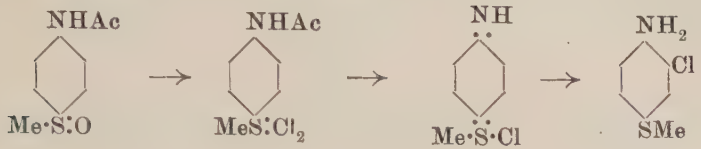
The latter alternative appears the more probable, but the evidence is not sufficiently decisive to warrant the exclusion of the anhydride structure. In this connexion it may be observed that it is customary to represent the analogous nitrogen compounds as phenol-betaines, and not as ammonium-quinones. The two series of compounds resemble one another very closely. The

[60] T. Zincke and J. Kempf, *Ber.*, 1911, **44**, 413; *A.*, i, 287.

[61] T. Zincke and R. Brune, *ibid.*, 1908, **41**, 902; *A.*, 1908, i, 336; also *ibid.*, 1911, **44**, 185; *A.*, i, 197.

[62] T. Zincke and R. Brune, *ibid.*, 1911, **44**, 187; *A.*, i, 197; see also T. Zincke and W. Glahn, *ibid.*, 1907, **40**, 3039; *A.*, 1907, i, 698.

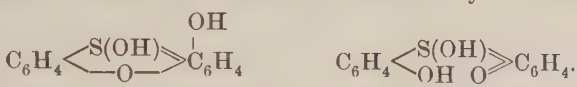
transitory existence of another type of sulphonium-quinone has been observed[63] in the interaction of hydrogen chloride with a *p*-acetylaminosulphoxide (I). In the first stage of the interaction a dichloride (II) is formed, but finally the chloro-amine (IV) is isolated, together with an unstable blue substance, to which the quinonoid structure (III) is assigned:



(I.) (II.) (III.) (IV.)

Here the assumption of the quinonoid structure is somewhat strengthened from analogy to the case of the *o*-sulphoxides of diphenylamine, which are successively converted by hydrogen chloride into the phenazothionium salt and chloro-amine.

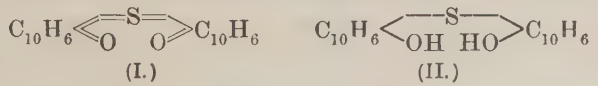
Another set of experiments[64] has dealt with diorthohydroxy-sulphoxides, which are converted by cold sulphuric acid into derivatives of phenothioxin (I). It is shown that the only satisfactory account of this interaction is furnished by the assumption



(I.) (II.)

that these sulphoxides behave towards acids like those of diphenylamine, and yield the sulphonium-quinones (II), which are subsequently converted into the cyclic compounds in question.

Taking a general view of the researches which have now been described, it appears that the simple benzenoid sulphonium-quinones are very unstable substances; but it seems probable that more stable derivatives of this type may be yet obtained by selecting particular conditions of the aromatic nucleus. A sign-post pointing in the required direction may be observed in the existence of β-naphthasulphonium-quinone (I). This constitution has been assigned[65] to the dehydrothio-β-naphthol which was obtained some years previously by treating β-naphthol sulphide (II) with mild

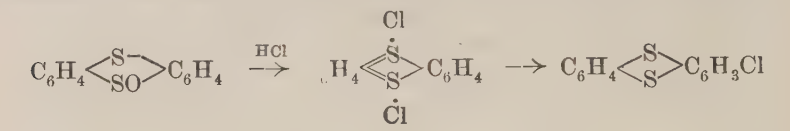


(I.) (II.)

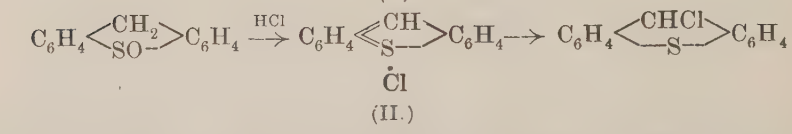
oxidising agents. It is a stable, although reactive, substance, and in many respects resembles β-naphthaquinone.

[63] T. Zincke and P. Jörg, *Ber.*, 1909, **42**, 3362; *A.*, 1909, i, 789.
[64] T. P. Hilditch and S. Smiles, *Trans.*, 1911, **99**, 973.
[65] T. P. Hilditch and S. Smiles, *loc. cit.*

A direct hint as to the manner in which the sulphonium-quinones may be obtained is given by the behaviour of certain cyclic sulphoxides. The ortho-sulphoxides of diphenylamine,[66] diphenyl-sulphide[67] (I), and of diphenylmethane[68] (II) yield the correspond-



(I.)



(II.)

ing sulphonium salts when treated with hydrogen chloride. These substances have been isolated, but they are not very stable, and under certain conditions readily pass into chloro-derivatives containing bivalent sulphur. In the series of diphenylamine and diphenyl sulphide, chlorination of the aromatic nucleus takes place, but with the sulphoxide of diphenylmethane the *meso*-chloro-derivative is formed. It has been shown that the formation of the sulphonium salts may be satisfactorily explained by assuming the separation of water or of hydrogen chloride from a salt of the sulphoxide; but with regard to the subsequent formation of the chloro-derivatives nothing definite is yet known, although it seems probable that the change involves some process similar to that suggested in the chlorination of aromatic *N*-acylamines.[69] Whatever the correct interpretation may be, it is noteworthy that the change is rendered more difficult, and the stability of the sulphonium salts consequently raised, by the insertion of halogen or of nitro-groups in the aromatic nuclei. With the simple amino-sulphoxide quoted on a previous page, it seems that the second or "chlorination" phase of the interaction proceeds too rapidly to permit the isolation of the sulphonium salt; but the remedy is obvious.

Finally, it may be observed that the conditions which determine the conversion of this type of sulphoxide into the sulphonium-quinone are by no means completely elucidated, for in some cases the change may be effected without the intervention of acid; for example, when β-naphthol sulphide is oxidised under conditions which in normal cases furnish the sulphoxide, the sulphonium-quinone is instead produced, whence it seems probable that the

[66] *Ann. Report*, 1910, .

[67] K. Fries and W. Vogt, *Annalen*, 1911, **381**, 312; *A.*, i, 555.

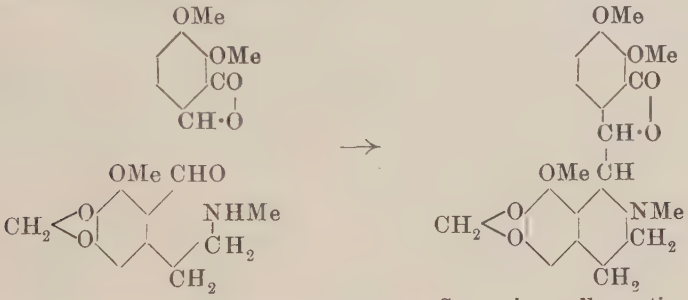
[68] T. P. Hilditch and S. Smiles, *Trans.*, 1911, **99**, 145.

[69] K. J. P. Orton, *Brit. Assoc. Report*, 1910.

former is unstable and tends spontaneously to yield the latter compound.

Alkaloids.

Among the researches carried out on this class of substances, those dealing with the *iso*quinoline group of alkaloids stand out more prominently. The synthesis of cotarnine which was effected [70] in 1910 has led to that of narcotine and gnoscopine.[71] Perkin has shown that the latter alkaloid may be directly synthesised from meconine and cotarnine merely by warming a mixture of those substances in alcoholic solution:



Gnoscopine or *dl*-narcotine.

The product is, of course, optically inactive, and it is identical with the naturally occurring gnoscopine; moreover, by resolution with α-bromocamphorsulphonic acid, narcotine was obtained, thus proving gnoscopine to be *dl*-narcotine, and confirming the opinion of Rabe,[72] who deduced this relation from the fact that gnoscopine is formed by boiling narcotine with aqueous alcohol.

Since the final step in the synthesis of alkaloids of the hydrastine and narcotine type turns upon the union of the meconine and cotarnine complexes, efforts are being made to discover the precise structural conditions which govern this reaction. The yields obtained in the synthesis of gnoscopine are poor, but experiments have shown that insertion of substituents such as halogen or the nitro-group into the meconine nucleus greatly facilitates the interaction. E. Hope and R. Robinson,[73] who have investigated the interaction of cotarnine with the simplest phthalide, have been led to the conclusion that the imino-group of cotarnine is an important factor in this condensation, and this opinion is supported by the work [74]

[70] A. H. Salway, *Trans.*, 1910, **97**, 1208.

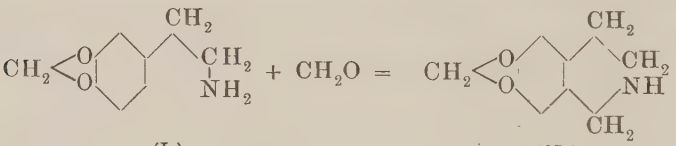
[71] W. H. Perkin, jun., and R. Robinson, *ibid.*, 1911, **99**, 775; *Proc.*, 1910, **26**, 46.

[72] P. Rabe and A. McMillan, *Ber.*, 1910, **43**, 800; *A.*, 1910, i, 335.

[73] *Trans.*, 1911, **99**, 1153; *Proc.*, 1910, **26**, 228.

[74] *Annalen*, 1910, **377**, 223; *A.*, i, 77.

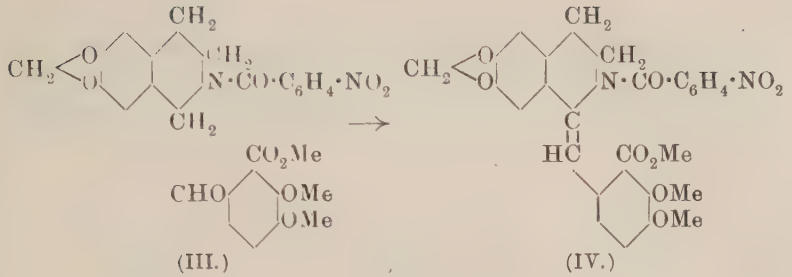
of Rabe and McMillan. The latter investigators, approaching the question from the opposite side, have studied the fission of the narcotine complex. Their experiments show that the condition of the nitrogen group is undoubtedly an important factor in determining the stability of union between the meconine and *iso*quinoline complexes. As previous experiments have frequently shown, these groups in narcotine and hydrastine are readily parted by the influence of alkaline reagents; but when the nitrogen in these substances is converted into the quaternary state by addition of methyl iodide, the carbon-chain remains intact, narceine or methyl hydrasteine being formed with alkalis. Pictet [75] has devised a very interesting method of synthesis for this group of alkaloids, and it has been successfully applied to oxyberberine. The process is accomplished in two distinct stages. The first consists of the production of the requisite *iso*quinoline derivative by a method [76] which apparently is of general application. Homopiperonylamine (I) is condensed with formaldehyde, and the product, norhydrohydrastine



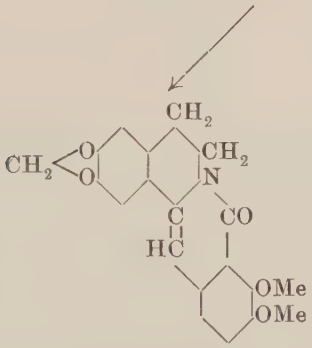
(I.) (II.)

(II), is converted by treatment with *o*-nitrobenzoyl chloride into the *N*-acyl derivative. In the second stage the latter substance is condensed with methyl opianate (III), the product (IV) being then treated with alcoholic potassium hydroxide. The resulting substance (V) was identical with oxyberberine. Attempts to reduce oxyberberine to berberine have not yet been successful:

[75] A. Pictet and A. Gams, *Ber.*, 1911, **44**, 2036; *A.*, i, 807.
[76] A. Pictet and T. Spengler, *ibid.*, 2030; *A.*, i, 750.

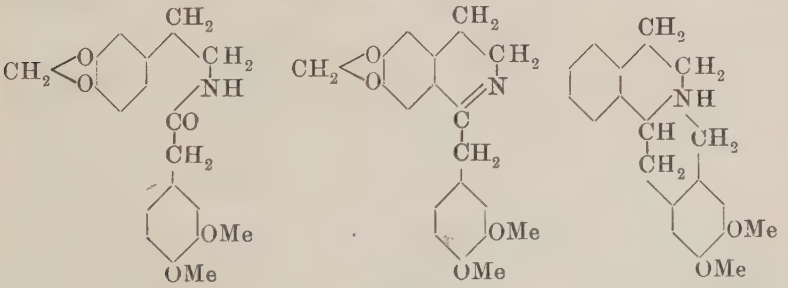


(III.) (IV.)



(V.)

On the other hand, tetrahydroberberine has been produced [77] by synthesis. The condensation product of homopiperonylamine and homoveratroyl chloride (VI) loses the elements of water when treated with dehydrating agents, furnishing the *iso*quinoline derivative (VII). The product obtained by reducing the latter is veratrylnorhydrohydrastinine, and this yields tetrahydroberberine



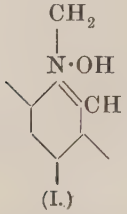
(VI.) (VII.) (VIII.)

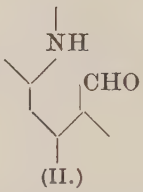
(VIII) on treatment with formaldehyde and hydrochloric acid. Previous work has shown that berberine is readily obtained from its tetrahydro-derivative by oxidation.

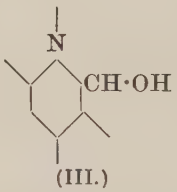
Although the main outlines of the structure now assigned to

[77] A. Pictet and A. Gams, *Compt. rend.*, 1911, **153**, 386 ; *A.*, i, 807.

berberine have been placed beyond question,[78] some doubt exists as to the form taken by the nitrogen group. There is general agreement that the salts are derived from the ammonium form, but for the free base selection must be made from the three formulæ now represented:


(I.)


(II.)


(III.)

The study of the absorption spectra of berberine[79] and certain derivatives of known structure seems to show that in solution the base may exist either as the ammonium hydroxide (I) or as the carbinol (III), according to the solvent chosen, the former being favoured by solvents such as alcohol or water, and the latter by ether, chloroform, or aqueous solutions of free alkali hydroxide. No evidence of the existence of the aldehydic form in solution could be obtained[80]; in fact, the case closely resembles that of cotarnine, which has been studied[81] by the same method. Before leaving this group of alkaloids mention must be made of the interesting hypothesis advanced by Pictet, that the *iso*quinoline derivatives occurring in plants[82] probably owe their origin to some process such as that followed in the interaction of formaldehyde and derivatives of β-phenylethylamine, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot NH_2$. It is noteworthy that this reaction takes place very readily with formaldehyde and phenylalanine, $C_6H_5 \cdot CH_2 \cdot CH(CO_2H) \cdot NH_2$, or tyrosine,

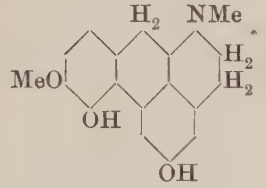
$$HO \cdot C_6H_4 \cdot CH_2 \cdot CH(CO_2H) \cdot NH_2,$$

both of which are found among the hydrolytic products of albuminoids. There is no doubt that of all the hypotheses advanced to explain the formation of *iso*quinoline derivatives in plants, the present is the simplest and most conformable to practical experience.

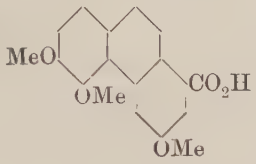
In the morphine group further progress has been made in elucidating the structure of the substances obtained by the interaction of these alkaloids with hydrochloric acid. The constitutions of

[78] See W. H. Perkin, jun., *Trans.*, 1889, **55**, 63; 1890, **57**, 992; 1910, **97**, 321.
[79] C. K. Tinkler, *ibid.*, 1911, **99**, 1340.
[80] See, however, W. H. Perkin, jun., *ibid.*, 1910, **97**, 321; A. Kaufmann and P. Strübin, *Ber.*, 1911, **44**, 680; *A.*, i, 321.
[81] J. J. Dobbie, A. Lauder, and C. K. Tinkler, *Trans.*, 1903, **85**, 598.
[82] A. Pictet and T. Spengler, *Ber.*, 1911, **44**, 2030; *A.*, i, 750.

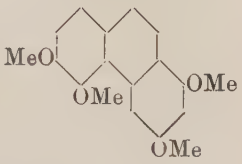
*apo*morphine [83] and of thebenine [84] have been successfully attacked in former years, and morphothebaine [85] has now yielded to similar methods. Previous work led to the suggestion of the following formula (I) for this substance:



(I.)

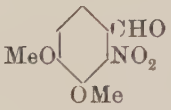


(II.)

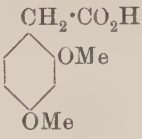


(III.)

Morphothebaine has been submitted to exhaustive methylation, and on oxidising the product a carboxylic acid was obtained, which was found to be derived from a trimethoxyphenanthrene. If the structure suggested for morphothebaine is correct, this acid must have the structure represented by (II), and when the carboxyl has been replaced by a methoxyl group [86] the product must be 3:4:6:8-tetramethoxyphenanthrene (III). Setting out from *o*-nitrovanillin methyl ether (IV) and 2:4-dimethoxyphenylacetic acid (V), Pschorr has succeeded in synthesising a substance of this



(IV.)



(V.)

structure, and it is identical with that obtained from morphothebaine; hence the suggested formula for this substance is confirmed. Other work in this group has been commenced with the object of attacking the constitution of morphine by breaking up the cyclic complex which contains the two ortho-hydroxyl groups. The preliminary stage in this investigation [87] appears to have been successfully accomplished by treating morphine in solution with nitrous vapours. An orange substance, probably a quinonitrol, is then formed, and this is decomposed by water into a carboxylic acid, which has been termed morphinic acid. The development of this attack will be interesting. Numerous interesting derivatives

[83] R. Pschorr, H. Einbeck, and O. Spangenberg, *Ber.*, 1907, **40**, 1998; *A.*, 1907, i, 635.

[84] R. Pschorr and H. Loewen, *Annalen*, 1910, **373**, 51; *A.*, 1910, i, 424.

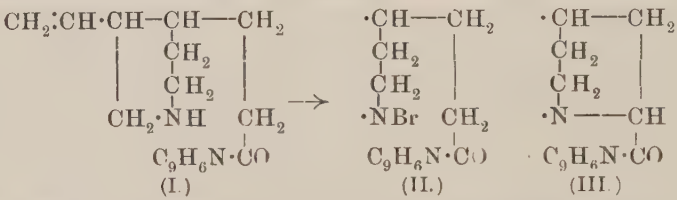
[85] R. Pschorr and G. Knöffler, *ibid*, 1911, **382**, 50; *A.*, i, 669.

[86] R. Pschorr and H. Rettberg, *ibid.*, 1910, **373**, 51; *A.*, 1910, i, 423.

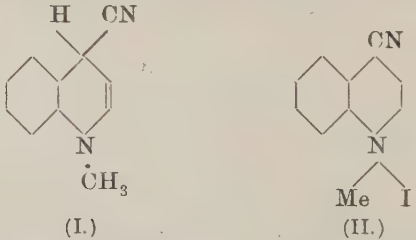
[87] H. Wieland and P. Kappelmeier, *ibid.*, 1911, **382**, 306; *A.*, i, 743.

of these alkaloids have been prepared,[88] but a detailed description of their behaviour is unnecessary, for this has not yet been brought to bear on the structure of the parent substances.

Turning to the group of cinchona alkaloids, we again find important progress in the work of synthesis. With the conversion of cinchotoxine into cinchoninone, Rabe[89] has accomplished the final stage of the synthesis of the bridged bicyclic system which characterises this group of alkaloids. Since the process is likely to be of importance in the complete synthesis of cinchonine, it may now be fully described. Cinchotoxine (I) when treated with hypobromous acid furnishes the *N*-bromo-derivative (II), which, in presence of sodium ethoxide, readily loses hydrogen bromide, being



converted into cinchoninone (III). Previous experiments[90] have shown that the ketone may be reduced to the secondary alcohol cinchonine. The same investigator has shown that oximinoquinotoxine[91] may be resolved into the nitrile of meroquinine and quinic acid, but since the process has been carried out some years previously with cinchotoxine (cinchonicine) no further comment is necessary. A synthesis of the quinoline portion of the cinchonine complex has been effected[92] by treating quinoline methiodide with potassium cyanide. The 4-cyano-derivative (I) which is then formed yields, on oxidation with iodine, the methiodide of 4-cyano-



quinoline (II). This may be further oxidised to the α-quinolone,

[88] M. Freund and E. Speyer, *Ber.*, 1911, **44**, 2339; *A.*, i, 909; L. Knorr and P. Roth, *ibid.*, 2754; *A.*, i, 1014; M. Freund and K. Lederer, *ibid.*, 2353; *A.*, i, 910.

[89] P. Rabe, *ibid.*, 2088; *A.*, i, 742.

[90] P. Rabe, *ibid.*, 1908, **41**, 67; *A.*, 1908, i, 100.

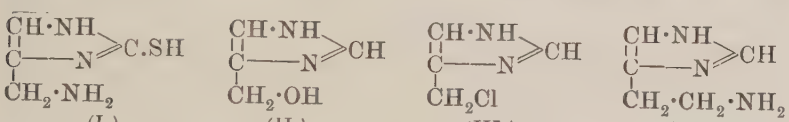
[91] P. Rabe and E. Milarch, *Annalen*, 1911, **382**, 365; *A.*, i, 741.

[92] A. Kaufmann and R. Widmer, *Ber.*, 1911, **44**, 2058; *A.*, i, 749.

which, on distillation with zinc dust, gives the nitrile of cinchonic acid. Other work has dealt[93] with the fluorescence of these alkaloids and their derivatives, and it has been found that the wave-length of the emitted light is influenced by slight changes in the constitution of the fluorescent molecule. In conclusion, it may be observed that those particularly interested in this group of alkaloids will find the subject admirably dealt with in a recent monograph.[94]

The recently discovered alkaloid, dioscorine, $C_{13}H_{19}O_2N$, has been submitted to a closer examination,[95] which has revealed the presence of a lactone ring and the imino-methyl group. Exhaustive methylation converts this substance into a hydrocarbon, $C_{11}H_{14}$, and this is considered to be a derivative of *cyclo*hexane, for, on addition of hydrogen bromide and removal of this substance with hot quinoline, another hydrocarbon is obtained which yields *o*-toluic acid on oxidation. A preliminary formula has been proposed to express these relations, as well as the fact that the physiological action of this alkaloid is similar to that of picrotoxine.

The physiological importance of the alkaloids containing the glyoxaline arrangement lends a general interest to the elegant syntheses recently effected in this group. The discovery[96] that the physiological behaviour of ergot is partly due to the powerful activity of an aminoethylglyoxaline has been rapidly followed by the synthesis of the compound.[97] The steps involved are too numerous to be represented fully in this place, and it must suffice to observe that the 2-thiol-4(or 5)-aminoethylglyoxaline (I) is obtained by interaction of potassium thiocyanate and diaminoacetone:



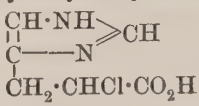
(I.) (II.) (III.) (IV.)

On treating this substance with nitric acid, the sulphur is eliminated, and the amino-group is replaced by hydroxyl; the product (II) yields the chloro-derivative (III) when submitted to interaction with hydrogen chloride. Thence, by means of potassium cyanide and subsequent reduction, 4(or 5)-β-aminoethylglyoxaline (IV) is obtained, the product being identical with that isolated from ergot.

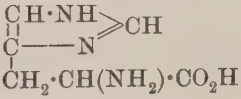
The chloro-derivative which is above formulated (III) has served

[93] P. Rabe and O. Marschall, *Annalen*, 1911, **382**, 360; *A.*, i, 741.
[94] Comanducci, *Sammlung. chemisch. Vorträge.*, 1911, **16**, 141.
[95] K. Gorter, *Rec. trav. chim.*, 1911, **30**, 161; *A.*, i, 222, 561.
[96] G. Barger and H. H. Dale, *Trans.*, 1909, **97**, 2592.
[97] F. L. Pyman, *ibid.*, 1911, **99**, 668.

as the starting point of the synthesis of histidine.[98] Thus, by heating it with ethyl sodiochloromalonate, an ester is formed, which may be hydrolysed, yielding the chloro-acid (V), and the latter, by



(V.)



(VI.)

treatment with concentrated aqueous ammonia, in turn furnishes racemic histidine (VI). This noteworthy synthesis has been rendered complete by the resolution of the inactive substance, and the lævo-isomeride was found to be the same as that obtained from natural sources. The synthesis of other important physiologically active substances in this group has been effected,[99] but considerations of space preclude a detailed account.

It remains to be mentioned that the structure of the alkaloid hypaphorine has been elucidated by the demonstration [1] that it is the betaine of tryptophane; in fact, the substance may be prepared by methylating tryptophane and decomposing the product with silver oxide.

Chlorophyll.

Apart from the isolation of the fundamental pyrrole derivatives, the main feature of the work dealing with chlorophyll and hæmatin has in the past been the preparation of a number of complex products of decomposition. To those not actually engaged in the work, the discovery of a large number of such derivatives and the lack of any definite information as to their nature naturally appears to obscure the few simpler facts already known with regard to the parental compounds. However, in the year now under review, Willstätter has so far succeeded in reducing to order the tangled mass of facts which hitherto represented the chemistry of chlorophyll, that a general outline may now be sketched of the chemical nature of that substance and of the relations of its decomposition-products.

The fresh material brought to bear on the discussion of the chemistry of chlorophyll has been obtained by two distinct lines of research; either by investigating the substances isolated together with chlorophyll in extracting the plant tissue, or by examining the degradation products obtained on attacking the chlorophyll nucleus with various reagents. The amorphous chlorophyll, which is obtained by extracting the natural material under carefully regu-

[98] F. L. Pyman, *Trans.*, 1911, **99**, 1386.
[99] G. Barger and A. J. Ewins, *ibid.*, 2336.
[1] P. van Romburgh and G. Barger, *ibid.*, 2068.

lated conditions, contains an unvarying amount—about 33 per cent. —of phytol.[2] The thoroughness with which this important relation has been established may be imagined from the fact that the chlorophyll from two hundred different kinds of plants has been compared. It may be observed in passing that the crystalline chlorophyll obtained by Borodin and others does not contain phytol, and it therefore cannot be the unaltered natural pigment.

The cautious hydrolysis of amorphous chlorophyll with cold dilute potassium hydroxide removes phytol and methyl alcohol, furnishing the potassium salt of a tricarboxylic acid which has been termed chlorophyllin. Hence it appears that the amorphous chlorophyll of nature is merely the di-ester of this chlorophyllin, in which two carboxyl groups are esterified by methyl alcohol and by phytol respectively,[3] the third probably remaining free. The relation between the two substances are represented as follows:

$$\begin{matrix} & CO_2H \\ C_{31}H_{29}N_4Mg & CO_2Me \\ & CO_2{\cdot}C_{20}H_{39} \end{matrix} \xrightarrow{\text{cold alkali}} C_{31}H_{29}N_4Mg(CO_2H)_3$$

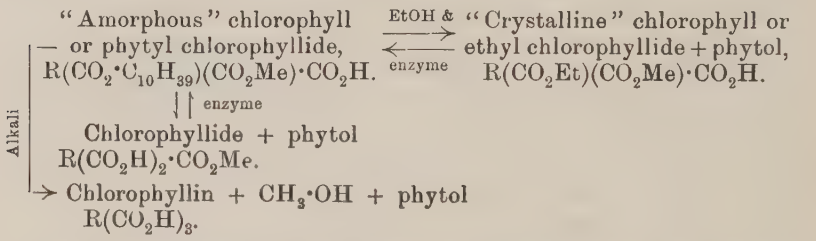
Amorphous chlorophyll. Chlorophyllin.

Of the two ethereal groups in question that containing the methyl is by far the more stable, so that by using other hydrolytic agents the phytolic residue may be removed, leaving the methyl chlorophyllin—a substance which is better known as chlorophyllide.

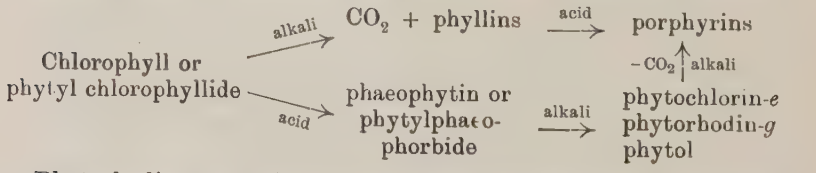
Further investigation has elucidated the nature of crystalline chlorophyll,[4] and its relation to the natural pigment. It has now been found that the crystalline substance does not contain two methoxyl groups as formerly supposed, but instead embraces methoxyl and ethoxyl in equivalent proportions. This at once furnishes a clue as to the method of its formation from amorphous chlorophyll, for it is prepared by extracting the plant substance with ethyl alcohol, and free phytol is always simultaneously obtained. There is now abundant proof to show that prolonged contact of the alcoholic solution of chlorophyll with the plant-substance permits the alcoholytic action of an enzyme, termed chlorophyllase,[5] which is contained in the latter. Experiments made with amorphous chlorophyll and chlorophyllase in ethereal solution show that phytol is readily eliminated by this enzyme, chlorophyllide being formed. If ethyl alcohol is used as the solvent, the liberated carboxyl group is re-esterified, giving ethyl chlorophyllide, and with methyl alcohol the new crystalline chlorophyll, methyl chlorophyllide, is produced. The ethyl chlorophyllide

[2] R. Willstätter and A. Oppé, *Annalen*, 1910, **378**, 1; *A.*, i, 140.
[3] R. Willstätter and A. Stoll, *ibid.*, 18; *A.*, i, 391.
[4] R. Willstätter and A. Stoll, *loc. cit.* [5] *Ibid.*

obtained in this manner is identical with the substance usually termed crystalline chlorophyll. Besides revealing these interesting relations, the researches with this group of substances have led to the synthesis[6] of chlorophyll from chlorophyllide and phytol by means of an enzyme, and there is scarcely room for doubt that the natural synthesis of the pigment takes place on these lines. A summary of the connexion between these substances is formulated below:


"Amorphous" chlorophyll — or phytyl chlorophyllide, $R(CO_2 \cdot C_{10}H_{39})(CO_2Me) \cdot CO_2H$.
EtOH & enzyme
"Crystalline" chlorophyll or ethyl chlorophyllide + phytol, $R(CO_2Et)(CO_2Me) \cdot CO_2H$.
enzyme
Alkali
Chlorophyllide + phytol $R(CO_2H)_2 \cdot CO_2Me$.
Chlorophyllin + $CH_3 \cdot OH$ + phytol $R(CO_2H)_3$.

The investigation of the behaviour of chlorophyll and other chlorophyllides with various hydrolytic agents has shown that either of two kinds of interaction may occur. Acid hydrolysis leads to elimination of the magnesium, whilst hydrolysis with alkali hydroxides leaves this metal intact and effects other changes in the chlorophyll nucleus. It is therefore clear that successive stages in the degradation of the complex may be attained by the consecutive application of these reagents, the intermediate substances obtained differing according to the order in which the application is made. For example, with alkali hydroxide under intensified conditions, phytyl chlorophyllide (chlorophyll) yields the "phyllins," and these with acid hydrolytic agents yield in turn the "porphyrins." On the other hand, if the chlorophyllide be first submitted to the interaction with acids, the "phaeophorbides" are produced, which are converted by mild alkaline hydrolysis into a mixture of "phytorhodin-*g*" and "phytochlorin-*e*." Finally, when "phytochlorin-*e*" is treated with hot alcoholic potassium hydroxide, carbonic acid is eliminated, and a member of the "porphyrin" series is produced.



Phytorhodin-*g* and phytochlorin-*e* have figured very prominently in the researches of the past year, and under close examination they have led to very important results. These substances are

[6] R. Willstätter and A. Stoll, *loc. cit.*

produced from all other known phaeophorbides which contain the chlorophyll nucleus free from magnesium:

Chlorophyllin	→ phaeophorbin	→	phytochlorin-*e*
Chlorophyllide	→ phaeophorbide	→	
Methyl chlorophyllide	→ methyl phaeophorbide	→	phytorhodir-*g*
Ethyl chlorophyllide	→ ethyl phaeophorbide	→	

and quantitative experiments[7] conducted with chlorophyllides of various origin have shown that the two compounds in question are always produced in the approximate ratio:

$$\frac{\text{phytochlorin-}e}{\text{phytorhodin-}g} = \frac{2{\cdot}5}{1}.$$

This circumstance may be interpreted either by supposing that the substances in question are contained in the required proportion by the chlorophyll molecule, or that they are separately produced by the hydrolysis of two kinds of the pigment. The former alternative must be rejected, for the molecular weight of either substance alone approximates to that of chlorophyll when allowance is made for the phytol and methyl alcohol contained therein. The conclusion thus reached as to the heterogeneity of the natural pigment is not by any means novel, for it has been previously advanced by several other workers, of whom, it may be noticed, Stokes was the earliest. However, definite proof has been now attained by the separation of a chlorophyll derivative into two components. The ethyl phaeophorbide, which is derived from "crystalline chlorophyll" by hydrolysis with cold acids, may be resolved by crystallisation[8] under special conditions into the *a* and *b* components. Moreover, it has been found that alkaline hydrolysis of the *a* and *b* ethyl phaeophorbides thus obtained yields respectively phytochlorin-*e* and phytorhodin-*g*. A similar separation, although not so complete, has been made with crystalline chlorophyll, which

Ethyl chlorophyllide, $C_{37}H_{39}O_{5\cdot5}N_4Mg$ → ethylphaeophorbide

a. $C_{37}H_{39}O_{5\cdot5}N_4Mg$. contains 50 % of a hydrate. $a : b = 2{\cdot}5 : 1$

b. $C_{37}H_{37}O_{6\cdot5}N_4Mg$.

a → Phytochlorin-*e* $C_{34}H_{34}O_5N_4$, also as hydrate (in varying proportions).

b → Phytorhodin-*g* $C_{34}H_{34}O_7N_4$

[7] R. Willstätter and M. Isler, *Annalen*, 1911, **380**, 154; *A.*, i, 392.

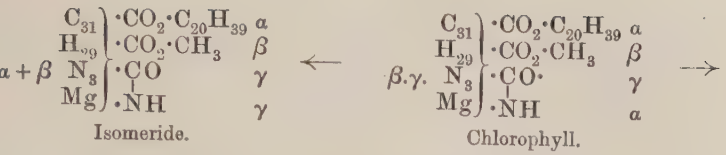
[8] R. Willstätter and M. Utzinger, *ibid.*, **382**, 129; *A.*, i, 659.

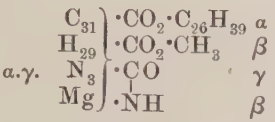
consists of the bluish-green *a* and the yellowish-green *b* forms. The scheme on p. 147 represents the connexion between these substances.

A clue to the relation between *a* and *b* chlorophyll has also been obtained. Since the final products of degradation of phytochlorin-*e* and phytorhodin-*g* are the same, it is evident that both contain the same general structure, which, according to the analytical data, must be present in either substance in a different stage of oxidation. With this conclusion as premise, it follows that the same relation holds between *a*- and *b*-chlorophylls, for there is no reason to suppose that oxidation or reduction occurs during the hydrolytic processes. This conception of the relation between the two chlorophylls is of importance, since it indicates that in the processes of assimilation the pigment may assume a chemical function in addition to the physical role which is usually ascribed to it.

Phytochlorin-*e* and phytorhodin-*g* are by no means the only degradation products of these types which have been isolated from chlorophyll, for by adopting different conditions of hydrolysis it is possible to obtain numerous isomerides.[9] To discuss in detail or even to enumerate the various cases would not only be inappropriate, but would also add confusion to a theme which is already sufficiently complex, for as yet the bearing of these substances on the constitution of chlorophyll remains somewhat obscure. The precise relations between the various phytorhodins and phytochlorins are not yet firmly established, but it may be noticed that the substances chiefly differ in their varying acidic or basic power. As Willstätter has pointed out, there is no doubt that the existence of so many isomerides is connected with the occurrence of three carboxyl groups and at least as many imino-groups in the chlorophyll complex. In chlorophyll itself, where two of the carboxyl groups are esterified with phytol and methyl alcohol, the third acid group almost certainly exists in the lactam arrangement ·CO·NH·, or the hydrated form thereof. It is therefore conceivable that under certain conditions the lactam system in chlorophyll might undergo fission and subsequent regeneration; moreover, if a different amino-group is involved in the new lactamic system, it is clear that an isomeric chlorophyll of different basic or acidic character will be formed. A graphic representation of this hypothesis is attempted in the following scheme; the different carboxyl and amino-groups are lettered accordingly:

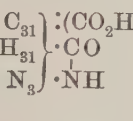
[9] R. Willstätter and M. Utzinger, *loc. cit.*



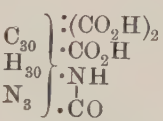


There is, indeed, experimental evidence in support of the hypothesis, for it is found when chlorophyll *a* has been kept for some time in light petroleum, that phytochlorin-*g* is formed [10] on hydrolysis, and not the *e*-isomeride, which is obtained from fresh material. Accordingly, there is no objection to assuming that the same kind of process may take place with alkaline reagents, and when it is considered that these liberate two other carboxyl groups the increased possibilities of isomerism at once become apparent. Moreover, it is clear that the nature of the alkali will, to a certain extent, determine which carboxyl and which amino-group will combine to give the lactam system.

At present all that can be tentatively said of the structures of the phytochlorins and phytorhodins is that they are respectively di- and tri-carboxylic derivatives of a complex which contains the lactamic and pyrrolic arrangements:



Phytochlorin.



Phytorhodin.

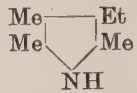
Thus it is seen that on passing from the "chlorin" to the "rhodin," a carbon group of the nucleus is oxidised to carboxyl; but it may be observed that this step has apparently not yet been realised in experiment.

Turning finally to consider the ultimate degradation products of this pigment, it is found [11] that reduction of the chlorophyll system by various methods yields a mixture of three pyrrole derivatives: hæmopyrrole, *iso*hæmopyrrole, and phyllopyrrole. The full evidence for the structures assigned to these compounds cannot be here

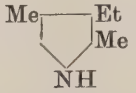
[10] R. Willstätter and M. Utzinger, *loc. cit.*

[11] R. Willstätter and Y. Asahima, *Annalen*, 1911, **385**, 188; *A.*, 1912, i, 41.

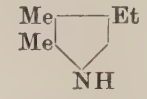
given; but it leads with apparent certainty to the following formulæ:



Phyllopyrrole.

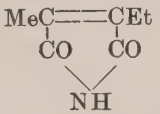


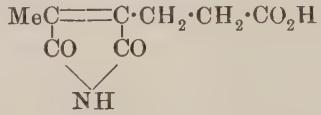
Hæmopyrrole.



*iso*Hæmopyrrole.

On the other hand, oxidising agents yield products[12] of acidic nature, such as methylethylmaleinimide and hæmatinic acid:





Hæmatinic acid.

In last year's report attention was drawn to the many points of resemblance between chlorophyll and hæmatin, and recent work has given emphasis to the likeness, for it has been found that the two hæmopyrroles and phyllopyrrole are also obtained by reducing hæmatin. With regard to the constitution of the latter, it may be observed that the accumulated data have proved sufficient for a detailed discussion of the question and for the establishment of a probable constitution for the substance. In this place more cannot be done than to refer the reader to the valuable summary of Piloty,[13] since most of the data contained therein have been previously published and discussed in the report of last year.

The foundation of any formula assigned to hæmatin and its congeners must be laid on the structures of phyllopyrrole and the hæmopyrroles, and it must be confessed that the present formulæ for these substances can only be accepted with some hesitation, in spite of the conclusive manner in which the analytical evidence favours them. The doubt arises from the recent synthetical experiments of Knorr,[14] who has prepared 2:4-dimethyl-3-ethylpyrrole (II) by reducing the hydrazone of 3-acetyl-2:4-dimethylpyrrole:

(I.) (II.)

The product was not identical with hæmopyrrole obtained from the natural pigment, although there was a strong resemblance between the two substances. To be obliged to leave the matter in this condition is somewhat unsatisfactory, but at the present state

[12] R. Willstätter and M. Utzinger, *loc. cit.*

[13] O. Piloty, *Annalen*, 1911, **377**, 314; *A.*, i, 92.

[14] L. Knorr and K. Hess, *Ber.*, 1911, **44**, 2758; *A.*, i, 1019.

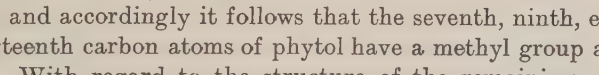
of affairs it is scarcely profitable to discuss the alternative ways out of the difficulty, and hence the satisfaction of presenting a more complete narrative must be left to a reporter of the future.

Attention has not been confined to the nitrogenous complex of chlorophyll, and the alcohol with which this is esterified has been very thoroughly examined.[15] The novel character and the importance of this substance offer some excuse for reviewing the chief facts which elucidate its constitution. Phytol, $C_{20}H_{39}\cdot OH$, is an unsaturated alcohol, and the situation of the ethylenic linking may be inferred from the products of oxidation with ozone or chromic acid. The latter-named reagent furnishes a mixture of phytenic acid, $C_{19}H_{37}\cdot CO_2H$, which contains the same number of carbon atoms as the alcohol, and a ketone of the formula $C_{15}H_{30}O$, whence it is evident that phytol is a primary alcohol, containing the ethenoid group between the fifth and sixth carbon atoms. Moreover, since phytenic acid readily yields a stable lactone, it appears that the unsaturated group is situated in the $\beta\gamma$-position with respect to the terminal carbon atom. Of the three alternatives for the arrangement of the first five carbon atoms, that outlined below is the most probable; the other two need not be here described, but

$$HO\cdot CH_2\cdot CHMe\cdot CMe{:}C_{15}H_{30}$$

the chief circumstance favouring that quoted is the occurrence of the same peculiar arrangement in other parts of the molecular structure. The ozonolysis of phytol yields a ketone, $C_{15}H_{30}O$, which may be transformed by a suitable process into the saturated acid, $C_{14}H_{28}O_2$, containing one carbon atom less; it therefore contains the ketomethyl, $\cdot CO\cdot CH_3$, arrangement. Further, when this ketone is treated with oxidising agents a series of three other ketones is obtained by successive removal of pairs of carbon atoms, together with acids which contain one carbon atom less than the ketonic products; thus it appears that these substances also are methyl ketones, and accordingly it follows that the seventh, ninth, eleventh, and thirteenth carbon atoms of phytol have a methyl group attached (see I). With regard to the structure of the remaining group of seven carbon atoms which is represented within the brackets in the

$$C_{15}H_{30}{:}CMe\cdot CHMe\cdot CH_2\cdot OH \longrightarrow C_{15}H_{30}O \text{ or } C_{13}H_{27}\cdot CO\cdot CH_3 \longrightarrow$$
$$C_{11}H_{23}\cdot CO\cdot CH_3 \longrightarrow C_9H_{19}\cdot CO\cdot CH_3 \longrightarrow C_7H_{15}\cdot CO\cdot CH_3$$



(I.)

above formula, nothing is yet known with certainty; but on general

[15] R. Willstätter, E. W. Meyer, and E. Hüni, *Annalen*, 1910, **378**, 73; *A.*, i, 144.

grounds the structure given seems probable. The methyl ketones which have been prepared from phytol are interesting, not only on account of their bearing on the structure of that substance, but also because of certain anomalies in their physical properties. An explanation of the latter has been sought in the assumption that the samples obtained consisted of the enolic isomerides.

This brief account of the investigation of phytol may be closed by mention of the hypothesis put forward to explain the natural synthesis of the substance. It has been pointed out that the peculiar structure of the alcohol suggests that it is formed by polymerisation of some hydrocarbon such as isoprene, four molecules being condensed by the intervention of water and hydrogen:

$$4C_5H_8 + H_2O + 3H_2 = C_{20}H_{40}O.$$

In spite of the slender basis on which this hypothesis lies, it is particularly attractive on account of the genetic connexion which it reveals between phytol and the terpenes, caoutchoucs, and other groups of compounds.

In concluding the report on organic chemistry it has almost become a rule to remark that much important work of the past year has not been reviewed. The omissions in the present case will certainly be evident to any who read the foregoing pages.

The writers, feeling that a compromise has of necessity been made, wish to point out that in making a choice of the subjects to be treated they have been guided by two motives: to choose from among the more important branches those in which sufficient progress has been made to form a connected story, and from the minor subjects to select those which appeared of a novel character or which enlisted their personal sympathies. The excuse for the latter mode of selection is that it has added something more of interest to the work.

F. D. Chattaway.
S. Smiles.

ANALYTICAL CHEMISTRY.

Reporters on the progress of analytical chemistry in other years have sufficiently emphasised the fact that in this branch of chemistry it is scarcely possible to fulfil the object of the Reports as set forth in the "Introduction" to Vol. I. (1904). Recognising this fact, the writer of this report has ventured to depart somewhat from the plan on which the corresponding report of previous years has been based. In the first place, fewer subjects have been treated of, but these few subjects have been treated at greater length, the number of references is much smaller, and a rather large proportion of these references are to papers published prior to 1911. This has necessitated the abandonment of the more minute subdivision of the subject adopted in recent years, for the writer has frankly abandoned the attempt to cover the whole ground of analytical chemistry. If, for example, no reference to water analysis is found, it must not be supposed that the writer holds the opinion that nothing useful has been accomplished in this branch during the year, but rather that he thinks this and other subjects can be treated in a more interesting and connected manner if left to the reporter of another year.

General.

An important communication has been made this year on the subject of melting-point determinations. It was the author's duty to recommend a standard apparatus and standard procedure for incorporation in the forthcoming United States Pharmacopœia, but his work has a more general value than this might suggest. In effect, he shows that the records of melting points, which are generally regarded as so important that they are copied into every journal of abstracts whatever else is omitted, are, in fact, of little value, and will remain of little value until some uniform method of determining melting points is agreed on. He also lays stress on the fact that a melting interval should always be reported. Although he is chiefly concerned with pharmaceutical preparations, which are often so far from pure that they exhibit a very wide

melting interval, there are a great many sharp melting points on record which no one except their authors has ever been able to confirm, working with the purest material obtainable. The general adoption of the custom of reporting a melting interval involves a definition of its beginning and ending, but this is not very difficult, as the paper under notice shows. The apparatus recommended by the author is of the simplest description.[1]

By means of Bousfield's pyknometer,[2] it is possible to determine the density of a liquid with an error of less than ± 1 in the fifth place of decimals, but some 250 c.c. of the liquid are required, and the degree of accuracy attained is, after all, not much in advance of that attained with quite astonishing rapidity by routine workers in laboratories where the densities of large numbers of dilute aqueous solutions have to be determined daily. It is now shown that a density determination accurate to ± 5 units in the sixth decimal place may be made with simple precautions, using no more than 25 c.c. of liquid.[3]

The investigation of capillarity constants, easily determined by Traube's dropping method, is one of the simplest of the physical methods applicable to analytical chemistry, but one which has been almost entirely neglected. The method should prove of special value for the detection of minute traces of colloid poisons and for the determination of adsorption-coefficients.[4]

This is presumably the place to call attention to a remarkable discourse delivered at the Royal Institution by Sir J. J. Thomson on a new method of chemical analysis. It is found that the positive rays with which the author has been working for some years afford a means of gaining an insight into the nature of the gases in a vacuum tube, and render possible a chemical analysis capable of determining whether, for example, oxygen is present, and, in addition, whether it is in the atomic or molecular condition or in more complex aggregations. The rays after passing through a fine tube in the cathode are exposed simultaneously to magnetic and electric forces, the former so arranged as to produce a vertical, the latter a horizontal, deflexion of the rays. When neither force is acting, the rays strike a point, O, on a screen placed at right angles to their direction, but under the influence of both fields strike another point, P. The length of the vertical line PN is proportional to the deflexion produced by the magnetic field, and that of the horizontal line ON to the deflexion produced by the

[1] G. A. Menge, *U.S. Treasury Dept., Hygienic Lab. Bulletin* 70.
[2] W. R. Bousfield, *Trans.*, 1908, **93**, 679.
[3] H. Hartley and W. H. Barrett, *ibid.*, 1911, **99**, 1072.
[4] I. Traube, *Ber.*, 1911, **44**, 556; *A.*, ii, 328.

electric field. It is known that $PN = Ae/v$ and $ON = Be/mv^2$, where A and B are constants depending on the strength of the fields and the geometrical data of the tube, e is the charge on the particle, m its mass, and v its velocity; then $\frac{m}{e} = \frac{A^2}{B} \cdot \frac{ON}{PN^2}$. When the rays strike a photographic plate, it is affected, and on development yields a permanent record of their deflexion. From the values for ON and PN obtained by measurement on the plates, one can determine the value of m/e, which for the same type of carrier is a constant, and this value can be compared for different rays by measuring the values of ON and PN. The locus of P is a parabola, and not a point, because the rays are not all moving with the same velocity, the slower ones suffering greater deflexion. Each type of carrier produces its own line on the plate, and there are as many curves on the plate as there are kinds of carriers, but, from the dimensions of the curves there can at once be calculated their atomic weights. It is in this last respect that the advantage of the new method over spectrum analysis is most obvious. The author shows how the application of the method to atmospheric nitrogen must have pointed to the existence of another gas with an atomic weight of 40, but the chief use of the method will, no doubt, be in the determination of atomic weights of forms of matter which have only a transient existence and exist in minute quantity only. The rays are registered within a millionth of a second of their formation, and the method will detect quantities of gas too minute to produce any indication in a spectroscope, whilst if as much as 0·01 milligram is available, an atomic-weight determination accurate to ± 1 per cent. is possible.[5]

From among a large number of pieces of new apparatus described within the year, attention may be called to an apparatus for the automatic extraction of aqueous liquids by means of specifically lighter solvents,[6] and to an apparatus for precipitating, filtering, and drying in an inert gas,[7] these being operations which many workers will be glad to find simplified for them.

In connexion with quantitative microchemical analysis, several useful pieces of apparatus have been devised, the most notable perhaps being a micro-filter,[8] and an apparatus for volumetric analysis with small quantities of liquid.[9]

[5] Sir J. J. Thomson, *Nature*, 1911, **86**, 466; compare also *Phil. Mag.*, 1911, [vi]. **21**, 225; *A.*, ii, 457.

[6] R. Kempf, *Chem. Zeit.*, 1910, **34**, 1365; *A.*, ii, 106.

[7] J. B. Firth and J. E. Myers, *Proc.*, 1911, **27**, 96.

[8] J. Donau, *Monatsh.*, 1911, **32**, 31; *A.*, ii, 225.

[9] F. Pilch, *ibid.*, 21; *A.*, ii, 225.

Gas Analysis.

None of the well-known methods for the determination of nitrous oxide in a gaseous mixture of which it is the principal constituent is quite satisfactory. Explosion with hydrogen may lead to results fully 2 per cent. below the truth, far too large an error when the object of analysis is to compare two commercial brands of compressed gas, of which few contain less than 95 per cent. and some over 99 per cent. of nitrous oxide. Exact results may be obtained by the following indirect method. A measured volume of the gas is passed over ignited copper gauze previously reduced in a current of hydrogen, and the current of gas is followed by one of hydrogen, the moisture formed during this second stage of the experiment being collected in a tared drying tube. The method, of course, measures not nitrous oxide alone, but the oxygen, free and combined, in the gas. In practice, however, the only correction usually necessary is that corresponding with the percentage of moisture of the gas, since commercial nitrous oxide appears to be free from compounds of oxygen other than nitrous oxide, and although oxygen itself can be detected in nearly every sample, its amount seems never to reach 0·1 per cent.[10]

Nitric oxide is absorbed completely and quickly when shaken in a Hempel pipette with a saturated solution of ferrous sulphate made faintly acid with sulphuric acid; but the method fails in presence of nitrous oxide on account of the high solubility of the latter gas in water, even when this is saturated with a salt such as ferrous sulphate. Previous saturation of the ferrous sulphate solution with nitrous oxide changes the large positive error to a small, but not insignificant, negative one, for the absorption of nitric oxide by the liquid reduces its capacity to hold nitrous oxide in solution, and this gas is set free. Divers' sodium sulphite method[11] possesses no advantages over the ferrous sulphate method, and the absorption is much slower. The gravimetric methods for the estimation of nitric oxide require such elaborate precautions to render them quantitative that they are rarely applicable. Among volumetric methods, that which makes use of permanganate has the advantage that this reagent is without action on nitrous oxide, but the apparatus recommended by Lunge[12] requires to have its air contents displaced by carbon dioxide, and this leads indirectly to errors which cannot be kept below 2 per cent. An apparatus has at last been designed which overcomes these difficulties, and

[10] C. Baskerville and R. Stevenson, *J. Ind. Eng. Chem.*, 1911, **3**, 579.
[11] E. Divers, *Trans.*, 1899, **75**, 82.
[12] G. Lunge, *Zeitsch. angew. Chem.*, 1890, **8**, 567.

by its aid the accurate estimation of nitric oxide becomes one of the easiest of analytical operations.[13]

A test capable of detecting as little as 0·05 c.c. of hydrogen in admixture with large volumes of other gases consists in passing the gaseous mixture through a solution of sodium molybdate contained in a test-tube, in which is also placed a piece of recently ignited platinum. The substitution of palladium for platinum increases the sensitiveness of the test, but requires certain precautions. If the gaseous mixture contains hydrogen, the liquid in the tube assumes a greenish-blue colour, a single bubble of pure hydrogen yielding an intense blue. The gas to be tested must be free from certain other gases, of which hydrogen sulphide and carbon monoxide are the most commonly occurring. Neither methane, ethylene, acetylene, nor their homologues interfere. Methods and apparatus have been described for concentrating on palladium sponge the hydrogen from large quantities of gas containing only minute traces of hydrogen, and subsequently demonstrating the presence of this hydrogen by means of the molybdate reagent.[14]

Inorganic Analysis.

Ebler has still further developed his method of qualitative analysis which avoids the use of hydrogen sulphide.[15] As originally described, it involved the use of a rather troublesome process for the separation of arsenic. It is now recommended that the separation of arsenic should be the first operation of analysis, and that it should be accomplished by distillation with hydrochloric acid and hydrazine bromide.[16] The directions for the treatment of insoluble residues have been modified so as to be applicable to complex cyanides, and so as to avoid the formation of insoluble substances of the type of chrome ironstone, which were occasionally formed when working according to the original scheme, and gave trouble in the subsequent analysis.[17] Another method of qualitative analysis which avoids the use of hydrogen sulphide is that of Pamfil,[18] but this requires much more elaboration before it can be recommended.[19]

Among qualitative reactions of the metals, the following perhaps

[13] L. Moser, *Zeitsch. anal. Chem.*, 1911, **50**, 401 ; *A.*, ii, 598.

[14] C. Zenghelis, *ibid.*, 1910, **49**, 729 ; *A.*, 1910, ii, 1106.

[15] E. Ebler, *Zeitsch. anorg. Chem.*, 1905, **48**, 61 ; *A.*, 1906, ii, 126 ; *Zeitsch. anal. Chem.*, 1908, **47**, 555.

[16] P. Jannasch and T. Seidel, *Ber.*, 1910, **43**, 1218 ; *A.*, 1910, ii, 1076.

[17] E. Ebler, *Zeitsch. anal. Chem.*, 1911, **50**, 603, 610 ; *A.*, ii, 932.

[18] G. P. Pamfil, *Mon. Sci.*, 1910, [iv], **24**, II, 641 ; *A.*, ii, 1030.

[19] D. A. Roche, *ibid.*, 1911, [v], **1**, I, 87 ; *A.*, ii, 1031.

deserve notice here. Titanium trichloride serves for the detection of one part of gold chloride in thirty million parts of water.[20] A solution of disodium 1:8-dihydroxynaphthalene-3:6-disulphonate serves to detect as little as 0·0008 milligram of chromium if present as chromate.[21] By the simultaneous action of nitrites and hyposulphites on solutions of nickel salts, a substance is formed which gives the solution a colour resembling permanganate. The colour is not given by cobalt salts, and is sufficiently intense to serve for the detection of nickel in presence of much cobalt.[22] Another reaction which serves for the differentiation of cobalt and nickel depends on the formation, in neutral solutions, of precipitates of basic chromate. The basic chromates of nickel and cobalt are both brown, but that of cobalt is much redder. However, their differentiation depends less on the colour of the precipitates than on the fact that the cobalt salt, unlike that of nickel, adheres firmly to glass vessels, and is precipitated even in the cold from comparatively dilute solutions.[23] A microchemical reaction of nickel and cobalt is referred to later in this report.

Possibly of more importance than any of these qualitative reactions is the observation that in ordinary systematic qualitative analysis it is impossible to detect small quantities of barium (up to 50 milligrams in a 1 gram sample) by ammonium carbonate, owing to losses which occur at various stages.[24]

Attention may be called to a useful paper in which a large number of reactions are described, which serve to distinguish between perborates, percarbonates, persulphates, perchlorates, and periodates.[25]

Among new microchemical reactions one may instance the use of dimethylaminobenzeneazobenzenesulphonic acid as a reagent for nickel and cobalt, the shape and size of the crystals of the nickel salt differing greatly from those of the cobalt salt formed under the same conditions.[26] Further notes have been published on the cæsium alum test for aluminium,[27] and on the use of ammonium uranyl acetate as a microchemical reagent for sodium,[28] which render these tests more delicate and certain.

[20] A. Stähler and F. Bachran, *Ber.*, 1911, **44**, 2906; *A.*, ii, 1096.
[21] P. Koenig, *Chem. Zeit.*, 1911, **35**, 277; *A.*, ii, 337.
[22] W. C. Ball, *Proc.*, 1910, **27**, 329.
[23] H. Weil, *Bull. Soc. chim.*, 1911, [iv] **9**, 20; *A.*, ii, 158.
[24] L. J. Curtman and E. Frankel, *J. Amer. Chem. Soc.*, 1911, **33**, 724; *A.*, ii, 659.
[25] W. Lenz and E. Richter, *Zeitsch. anal. Chem.*, 1911, **50**, 537; *A.*, ii, 823.
[26] M. E. Pozzi-Escot, *Bull. Soc. chim.*, 1911, [iv], **9**, 22.
[27] N. Schoorl, *Zeitsch. anal. Chem.*, 1911, **50**, 266; *Chem. Weekblad*, 1911, **8**, 268; *A.*, ii, 443.
[28] W. Lenz and N. Schoorl, *Zeitsch. anal. Chem.*, 1911, **50**, 263; *Chem. Weekblad*, 1911, **8**, 266; *A.*, ii, 439.

So far as the quantitative determination of anions is concerned, the year under review has produced no work equal in importance to that of Allen and Johnston on the exact determination of sulphate. Formerly regarded as one of the most exact methods at the disposal of the analyst, it has been recognised for some years that the estimation of sulphate as barium sulphate holds sources of error which are quite large, and that the degree of accuracy often, but by no means invariably, attained in practice depends on a partial compensation of errors, opposite in sign. Beyond that, until last year nearly every statement in the literature was misleading, authors appearing to have no other object in view than the general adoption of their own empirical method. It is now known that *plus* errors may be entirely avoided, whilst the sources of the *minus* ones have been traced, with the result that these can be kept low, and accurate corrections made for such error as cannot be avoided. The solubility of barium sulphate in very dilute hydrochloric acid is small, and, contrary to many published statements, is almost independent of the amount of alkali chloride present. Alkali chloride, present in most sulphate determinations and often present in very large amount, is, however, the chief source of error. All barium sulphate precipitates carry down with them quantities of alkali sulphates. In the case of pure acidulated sulphates, this quantity is not far from 0·5 per cent., corresponding with an error of 0·35 per cent. if the sulphate be that of sodium, whilst the error due to this cause may be doubled if alkali chlorides are present in quantity. Barium sulphate, when precipitated from acidulated solutions of alkali sulphates, always occludes a certain amount of "free" sulphuric acid. High concentrations of acid increase the amount of sulphuric acid occluded, and alkali chlorides increase it so much that, where they are present in large amount, it is the chief source of error. All barium sulphate precipitates contain barium chloride. Compensation methods depend on this, but, since the compensating errors are large and their exact amount dependent on conditions difficult to control except in routine work on comparatively uniform material, it is far better, as it is quite easy, to reduce this positive error to negligible proportions. If the precipitation be made slowly, the precipitate does not contain more than 0·15 per cent. of barium chloride, and all but a trace of this is eliminated during ignition, the barium combining with the "free" sulphuric acid always present in more than equivalent quantity. On these observations an exact method has been worked out for the determination of sulphate under any conditions. It is a tedious method, involving the use of large quantities of material and the subsequent experi-

mental determination of certain corrections,[29] but for work making any pretence to scientific accuracy and for commercial referee work, except where some empirical method is specified in the contract, these would seem to be an obligation on the analyst to adopt this method, or at least to work with due regard to the facts its authors have established. During the present year attempts have been made, in the light of the above-recorded results, to find a direct method for the determination of sulphate, which should be generally applicable, exact, and require only small and easily determined corrections. There appears to be little chance of discovering an exact method which shall be generally applicable and require no corrections, and yet not owe its accuracy to a compensation of errors. Where, however, the composition of the solution is approximately known—a condition which frequently obtains in practice—recourse may be had to a calibration method. Such a method, yielding results accurate to 0·05 per cent., has been worked out. It depends on keeping the individual errors as small as possible, and correcting for these by running a concurrent determination on a known and approximately equal weight of pure potassium or sodium sulphate in a medium such that the resulting solution is as nearly as possible of the same composition as the solution to be analysed.[30]

The distillation methods for the estimation of fluorine being tedious, a precipitation method sufficiently exact for many purposes is a matter of interest. It depends on the comparative insolubility of lead chlorofluoride, PbFCl, in water, and its still more marked insolubility in solutions of lead chloride. The solubility is not so low as could be wished in a compound chosen to serve as the basis of an analytical method, but quantities like 0·03 gram of fluorine can be determined with an error not exceeding ± 1 per cent., and this without any correction based on the known solubility of the precipitate in the liquids used for washing or on parallel experiments with known quantities of fluoride. An advantage of the method is the high ratio of the weight of the precipitate to the weight of fluorine estimated.[31]

An interesting method for the estimation of nitrite nitrogen depends on the use of hydrazine sulphate. When excess of the latter is allowed to act on a solution of any ionised nitrite, nitrogen, nitrous oxide, and ammonia result, in accordance with the following equation:

$$2NH_2{\cdot}NH_2 + 3ON{\cdot}OH = NH_3 + 2N_2O + N_2 + 4H_2O.$$

[29] E. T. Allen and J. Johnston, *J. Amer. Chem. Soc.*, 1910, **32**, 588; *A.*, 1910, ii, 650; *J. Ind. Eng. Chem.*, 1900, **2**, 196.

[30] J. Johnston and L. H. Adams, *J. Amer. Chem. Soc.*, 1911, **33**, 829; *A.*, ii, 766.

[31] G. Starck, *Zeitsch. anorg. Chem.*, 1911, **70**, 173; *A.*, ii, 436.

If the reaction is allowed to take place in a nitrometer, the nitrous oxide may be removed by washing with water, and the residual nitrogen measured. The method has been successfully applied to some fifty nitrites, including tetramethylammonium nitrite and benzylamine nitrite, as well as the nitrites of the alkalis, alkali earths, and heavy metals. On the other hand, amyl nitrite, and in general non-ionised nitrites, do not give rise to any evolution of gas when brought in contact with hydrazine sulphate.[32]

A method has been described for estimating the activity of oxidising agents by means of the quinonoid imonium salts of benzidine. If an oxidising agent be added to an excess of an aqueous solution of benzidine, a blue precipitate, insoluble in dilute saline solutions and sparingly soluble in water, is obtained. This compound is an analogue of the *meri*-quinonoid salts of diphenoquinonedi-imine described by Schlenk, the negative radicle depending on the particular oxidising agent employed. Since the compound retains in the active form the whole of the oxidising power of the active oxygen employed in its formation, it affords a means of estimating the oxidising power of solutions obtained in the course of physiological investigations and of coloured solutions which cannot be titrated direct. The blue compound is filtered off, decomposed with hydrochloric acid, and treated with potassium iodide, the liberated iodine being subsequently titrated with thiosulphate. The method has been chiefly used in the investigation of blood and of peroxydases, and might equally well have found mention in a later section of this report, but is assigned its present place because of the probability that the mechanism of the action of oxydases, peroxydases, and catalases rests on an inorganic basis.[33]

A critical investigation of the volumetric methods for the estimation of mercury depending on reduction to metal has led to the recommendation of a modification of Feit's method.[34] The new method surpasses any of its predecessors in accuracy, but, like Feit's original method, has the disadvantage that the mercury in the solution to be tested must all be in the mercuric state. The mercury is obtained in globules of such a size that solution of mercury by iodine is very slow. This makes it possible to avoid filtration without diminution of accuracy. The accuracy attainable is within 0·05 c.c. of the solutions used, and is secured by carrying

[32] B. B. Dey and H. K. Sen, *Zeitsch. anorg. Chem.*, 1911, **71**, 236 ; *A.*, ii, 822.

[33] W. Madelung, *Ber.*, 1911, **44**, 626 ; *A.*, i, 323 ; *Zeitsch. physiol. Chem.*, 1911, **71**, 204 ; *A.*, i, 411.

[34] W. Feit, *Zeitsch. anal. Chem.*, 1889, **28**, 318 ; *A.*, 1889, 927.

out the reduction by means of sodium arsenite in a non-oxidising atmosphere.[35] The method is less rapid than that of Rupp,[36] and Rupp's method has the advantage that it is applicable to mixtures of mercuric and mercurous salts, which are first reduced to metal by some reducing agent without action on iodine in acid solution, the mercury being then dissolved by excess of standard iodine solution, and the excess of iodine determined by means of thiosulphate. As originally described, however, Rupp's method does not yield results of the highest accuracy, and the modifications of it (for example, that of Muller[37]) complicate it without notable improvement in the accuracy of the results.

A portion of the copper in burned pyrites obstinately resists solution by means of nitric acid, but the whole of the copper in either pyrites or burned pyrites may be obtained in solution suitable for electrolysis after heating for a few minutes with reduced iron in an ignition tube. The contents of the tube are treated with hydrochloric acid until all the iron is dissolved, and any copper not already precipitated as sulphide is thrown down by means of hydrogen sulphide. The insoluble matter is then collected and washed, and the copper brought into solution suitable for electrolysis.[38]

A method described by Heath for the estimation of arsenic in copper will appeal to too narrow a circle to justify more than mere mention here, but there can be no doubt that it surpasses all older methods in accuracy.[39]

The separate estimation of tin and antimony when occurring together in solution ceased to be a difficult operation with the appearance of Low's method[40] in 1907. The operation of dissolving tin from its ores appears still to give trouble to many workers, and for this reason attention may be directed to two recent notes.[41] Although the existence of Low's method deprives new methods for the estimation of tin and antimony of much of the interest which would formerly have attached to them, attention must be called to one recent method which is wholly novel and almost as simple as that of Low. It depends on the fact that, in acid solution, both stannic and stannous sulphide yield stannic iodide on treatment with iodine, whilst both antimonous and antimonic sulphide yield

[35] F. Reinthaler, *Chem. Zeit.*, 1911, **35**, 593 ; *A.*, ii, 660.
[36] E. Rupp, *Arch. Pharm.*, 1905, **243**, 300 ; *A.*, 1905, ii, 484.
[37] J. A. Muller, *Bull. Soc. chim.*, 1907, [iv], **1**, 1169 ; *A.*, 1908, ii, 227.
[38] W. N. Iwanoff, *Chem. Zeit.*, 1911, **35**, 551 ; *A.*, ii, 660.
[39] G. L. Heath, *J. Ind. Eng. Chem.*, 1911, **3**, 74.
[40] W. H. Low, *J. Amer. Chem. Soc.*, 1907, **29**, 66 ; *A.*, 1907, ii, 304.
[41] H. Y. Loram, *Proc.*, 1911, **27**, 60 ; A. Gilbert, *Zeitsch. öffentl. Chem.*, 1910, **16**, 144 ; *A.*, ii, 71.

antimonous iodide, the whole of the sulphur separating as such if iodine is present in excess.[42]

For the estimation of chromium in steels which also contain tungsten, the most accurate method is that of von Knorre,[43] but it is somewhat tedious, and calls for the continuous attention of an experienced operator. Means have been found to simplify it so that the analysis may be completed in less than two hours, an advantage which may in many cases outweigh the slight decrease in the accuracy of the results.[44] The reaction of chromates with disodium 1 : 8-dihydroxynaphthalene-3 : 6-disulphonate, referred to among qualitative reactions, may be made the basis of a colorimetric method for the estimation of extremely minute quantities of chromium.[45]

Although manganese is usually estimated by volumetric methods to-day, a paper which lays down the conditions under which MnO, Mn_2O_3, or Mn_3O_4 can be completely converted into either of the other oxides must be regarded as important.[46] With so many good methods available for the estimation of manganese, no great importance attaches to a new one, unless the authors are right in thinking that for certain steels it gives results slightly more accurate than those obtained by other methods. It depends on the fact that, in presence of sufficient hydrofluoric acid, manganese reacts quantitatively with permanganate, all the manganese after the reaction being in the tervalent form.[47]

Several papers have appeared during the year on the estimation of small quantities of lime in presence of much magnesia, but the method of Murmann remains the only satisfactory method where the magnesia-lime ratio exceeds 50 : 1. The method depends on the insolubility of calcium sulphate in 90 per cent. alcohol, and judged from some abstracts of the paper might appear indistinguishable from a method to be found in many text-books. Reference to the original, however, will show that this is no purposeless modification.[48] The same author has worked out a simpler method, which gives results sufficiently accurate for many technical purposes when the magnesia-lime ratio is less than that stated. Essentially it consists in the substitution of quinoline for ammonia in the ordinary oxalate precipitation.[49]

[42] J. C. Beneker, *J. Ind. Eng. Chem.*, 1911, **3**, 637.
[43] G. v. Knorre, *Stahl u. Eisen*, 1907, **27**, 1251.
[44] H. Wdowiszewski, *Chem. Zeit.*, 1910, **34**, 1365 ; *A.*, ii, 157.
[45] P. Koenig, *loc. cit.*, and *Landw. Jahrb.*, 1910, **39**, 775 ; *A.*, ii, 524.
[46] P. N. Raikow and P. Tischkoff, *Chem. Zeit.*, 1911, **35**, 1013 ; *A.*, ii, 936.
[47] F. J. Metzger and L. E. Marrs, *J. Ind. Eng. Chem.*, 1911, **3**, 333.
[48] E. Murmann, *Zeitsch. anal. Chem.*, 1910, **49**, 688 ; *A.*, 1910, ii, 897.
[49] E. Murmann, *Monatsh.*, 1911, **32**, 105 ; *A.*, ii, 440.

Rawson's method for the separation of strontium from calcium[50] has been finally discredited, and the opinion expressed that the ether-alcohol method alone of existing methods has any claim to exactness.[51] Many will endorse this view, but almost simultaneously a method was described which depends on the insolubility of strontium chromate in 50 per cent. alcohol. If this method proves sound, it will become important, as it forms part of a method for the separation of barium, strontium, and calcium which is capable of a volumetric modification.[52] A method has been described for the separation of barium from calcium and magnesium by the action of acetyl chloride and acetone on the mixed chlorides.[53]

Following up the work of Rothe, whose process for the ether separation of iron[54] from other metals has proved so valuable in working out methods for the analysis of special steels, Mylius and Hüttner have studied the behaviour of thirteen metallic chlorides when shaken with ether and water or with ether and hydrochloric acid of varying strength.[55] The immediate result of this research is the elaboration of a new wet method for the assay of gold bullion. Four or five extractions with ether suffice to obtain results accurate to 1 per mille. For the most exact work of a mint, the ether process is made use of to separate the bulk of the gold from all the other metals. These and traces of gold are then recovered from the acid-aqueous solution by the usual methods. The method diminishes the tediousness of a complete analysis of gold bullion, and in point of accuracy cannot be excelled, but its practical value depends perhaps more on the fact that it affords the most ready means of preparing normal gold of the highest grade of purity.[56]

The iodic acid method for the separation of thorium[57] has been further studied, as well as the conditions which determine its successful application to the detection of traces of thorium in presence of much cerium. In its improved form the method affords a means of separating scandium from thorium.[58]

A method has been described for the separation of columbium, tantalum, titanium, and tungsten from the rare earth metals which

[50] C. Rawson, *J. Soc. Chem. Ind.*, 1897, **16**, 113.

[51] L. Moser and L. Machiedo, *Chem. Zeit.*, 1911, **35**, 337; *A.*, ii, 439.

[52] J. L. M. van der Horn van den Bos, *Chem. Weekblad*, 1911, **8**, 5; *A.*, ii, 228.

[53] F. A. Gooch and C. N. Boynton, *Zeitsch. anorg. Chem.*, 1911, **70**, 400; *A.*, ii, 334.

[54] T. W. Rothe, *Mitt. d. Kgl. Techn. Versuchsamt.*, 1892, 132.

[55] F. Mylius and C. Hüttner, *Ber.*, 1911, **44**, 1315; *A.*, ii, 540.

[56] F. Mylius, *Zeitsch. anorg. Chem.*, 1911, **70**, 203; *A.*, ii, 444.

[57] R. J. Meyer and M. Speter, *Chem. Zeit.*, 1910, **34**, 306; *A.*, 1910, ii, 459.

[58] R. J. Meyer, *Zeitsch. anorg. Chem.*, 1911, **71**, 65; *A.*, ii, 825.

depends on the fact that the former may be volatilised as chlorides in a current of sulphur monochloride.[59]

It has been shown that the uncertain end-point in the titration of ferrous iron in silicate rocks after decomposition of the rock by means of hydrofluoric and sulphuric acids is unconnected with the presence of manganese, and that the usual precautions fail to make the end-point even reasonably sharp with some rocks. These rocks were in every case found to contain notable proportions of titanium, but titanium dioxide, even in large amount, has no disturbing effect on the titration. Addition of titanous acid, however, to a ferrous solution before titration with permanganate, leads, as might be expected, to indefinite end-points similar to those occasionally observed in the course of rock analysis. It is suggested that rocks may contain titanium as Ti_2O_3, as well as in one or other of the crystalline modifications of the dioxide. This view is confirmed by the fact that sharp end-reactions may be obtained by the addition to the titration liquid of excess of finely divided silica and a considerable amount of potassium sulphate. Ferric salts are but slowly reduced by titanous acid in hydrofluosilicic acid solution, and high saline concentrations also tend to retard the reaction.[60]

It is now generally recognised that the exact determination of vanadium, especially in chrome vanadium steels, is a far less easy operation than might be supposed on reference to papers not many years old. Methods requiring the use of ferricyanide as indicator for ferrous salts, where quadrivalent vanadium and ferric salts are also present, must of necessity be very uncertain. An error in all methods where final titration is made against permanganate may arise by failure to deduct the blank due to elements other than vanadium. This error may amount to 100 per cent. in the case of products of low vanadium content. The temperature of titration is also important. In methods in which iron is removed by ether extraction, ferrous salts are apt to be formed, and must be re-oxidised. If the evaporation of a solution of quadrivalent vanadium with concentrated sulphuric acid, to eliminate hydrogen chloride, is too prolonged or conducted at too high a temperature, oxidation may occur.[61] In methods in which, after an ether separation, the remainder of the iron, as well as any chromium, is to be separated from vanadium by pouring into a boiling solution of alkali hydroxide, there are several sources of possible error. Vanadium is almost always carried down with the hydroxides of iron and chromium, and two or three precipitations are necessary.

[59] W. B Hicks, *J. Amer. Chem. Soc.*, 1911, **33**, 1492 ; *A.*, ii, 567.
[60] M. Dittrich, *Chem. Zeit.*, 1911, **35**, 1093 ; compare *A.*, ii, 543.
[61] E. Müller and O. Diefenthäler, *Zeitsch. anorg. Chem.*, 1911, **71**, 243 ; *A.*, ii, 824.

Another source of error is due to manganese, which tends to become oxidised to peroxide during the boiling with alkali hydroxide, and this peroxide oxidises chromium salts to chromate. Some, but not all, of these errors are avoidable, and it will be apparent that agreement between laboratories using different methods must depend in large measure on the exchange of "analysed samples." Such "analysed samples," especially when they can be obtained by everyone, as in the case of those issued by the United States Bureau of Standards, are useful, but they are a poor substitute for an exact method. An exact method appears now to be available to those who possess electrolytic appliances. Vanadium and chromium are precipitated together with a little iron by adding a large excess of cadmium carbonate to the boiling acid solution. The precipitate is dissolved in acid, freed from cadmium by means of hydrogen sulphide, and the filtrate electrolysed, using a mercury cathode, until free from iron and chromium. In the exhausted electrolyte the determination of vanadium is easy.[62]

The tendency of precipitates of ferric hydroxide to carry down vanadium, referred to above as a fertile source of error in determinations of vanadium, is actually made use of in one recently described method. The method is available in presence of chromium, but it is a colorimetric method, and therefore of limited accuracy, and it requires the preparation of standards containing approximately the same amount of iron and acid as the solution under examination.[63]

A new, rapid, and accurate method for the volumetric estimation of molybdenum, depending on its reduction by zinc and hydrochloric acid and the subsequent oxidation of the reduced solution with standard methylene-blue, is deserving of notice, but it is not applicable to the analysis of steels containing titanium, tungsten, chromium, or vanadium.[64] As our knowledge grows, the choice of methods for the determination of molybdenum in actual practice tends to decrease; for example, molybdenum glance now comes into the market containing notable amounts of magnesium, copper, and zinc, nearly the whole of which may get weighed as MoO_3 when the material is analysed in accordance with the directions to be found in some recent text-books. For such material the method of Trautmann [65] appears the only one available, and all but experienced

[62] J. R. Cain, *J. Ind. Eng. Chem.*, 1911, **3**, 476.

[63] C. R. M'Cabe, *Chem. Engineer*, 1911, **13**, 243; *Chem. News*, 1911, **104**, 194, 202.

[64] E. Knecht and F. W. Atack, *Analyst*, 1911, **36**, 98; *A.*, ii, 337.

[65] W. Trautmann, *Chem. Zeit.*, 1909, **33**, 1106; *A.*, 1909, ii, 942; *Zeitsch. angew. Chem.*, 1911, **24**, 207; *A.*, ii, 230.

workers will do well to weigh finally as MoS_2, as suggested by Collett and Eckardt.[66]

Several methods are available for the accurate determination of tungsten in wolfram concentrate, and useful notes on each have been published within the year.[67] A volumetric method applicable to the analysis of commercial tungstic acid and to lamp filaments has also been described.[68] The authors of the latter claim that their method is available for the rapid and exact determination of tungsten in steel, but give no test numbers for a chrome-tungsten steel. If the method proves accurate for chrome-tungsten steel, it will assume considerable importance for the best existing method —von Knorre's benzidine method[69]—cannot be described as more than fairly satisfactory.[70]

The use of alloys of tungsten, molybdenum, vanadium, etc., by steel-makers has not only necessitated a strict re-investigation of methods for the estimation of these elements, but has also considerably complicated the determination of carbon, sulphur, and phosphorus in steel and steel-works materials. As examples only of work in this direction, attention may be called to the recent statements that, in high-grade alloys of tungsten, molybdenum, or vanadium with iron, carbon and sulphur can be determined accurately only by direct dry combustion[71]; that, in ferrotitanium alloys containing much silicon, carbon cannot be determined accurately by direct combustion unless the alloy be first decomposed in a current of chlorine[72]; and to a paper on the estimation of phosphorus in tungsten steel.[73]

It has been proposed to make use of sodium thiosulphate as standard in alkalimetry. The proposal rests on the fact that when excess of mercuric chloride is allowed to act on thiosulphate, two molecules of hydrogen chloride are set free by each molecule of thiosulphate present.[74]

[66] E. Collett and M. Eckardt, *Chem. Zeit.*, 1909, **33**, 968; *A.*, 1909, ii, 941.
[67] H. W. Hutchin, *Analyst*, 1911, **36**, 398; *A.*, ii, 940.
[68] E. Knecht and Miss E. Hibbert, *ibid.*, 96.
[69] G. v. Knorre, *Zeitsch. anal. Chem.*, 1908, **47**, 337; *A.*, 1908, ii, 779.
[70] F. W. Hinrichsen and T. Dieckmann, *Mitt. K. Materialprüfungsamt Gross-Lichterfelde West*, 1910, **28**, 229; *A.*, ii, 156.
[71] E. Müller and B. Diethelm, *Zeitsch. angew. Chem.*, 1910, **23**, 2114; *A.*, 1910, ii, 1110.
[72] W. Trautmann, *ibid.*, 1911, **24**, 877; *A.*, ii, 661.
[73] F. W. Hinrichsen, *7th Intern. Congr. App. Chem.*, 1909, I, 116.
[74] W. Feld, *Zeitsch. angew. Chem.*, 1911, **29**, 1161; *A.*, ii, 769.

Electrochemical Analysis.

Whilst much careful and useful work is accomplished each year, so far as the determination of metals is concerned, the advance to be recorded is mainly one of detail, which can find no notice here. The work of Stoddard[75] with the mercury cathode and stationary anode, however, seemed to herald a reaction towards simpler forms of apparatus. Benner and others have not only confirmed the work of Stoddard,[76] but have shown that rapid and accurate work can be accomplished by means of a stationary anode and gauze cathode.[77] Other proposals to dispense with mechanical agitation depend on the use of special but simple apparatus. According to one of these proposals, the electrolyte is agitated by means of a current of gas,[78] whilst, according to another, agitation is effected by the gas evolved during electrolysis, the volume of this gas being made sufficient for the purpose by working under diminished pressure.[79] If attention is directed to work of this kind rather than to work of the type represented by a paper of Sand,[80] it is because work of the latter kind will necessarily be read by all who are actually engaged in electrochemical analysis, whilst a perusal of the papers quoted may cause some to reconsider an aversion to electrochemical methods engendered by the increasing complexity of the apparatus recommended in recent years.

Where it can be shown that results of the highest order of accuracy cannot be obtained by simpler means, no amount of complexity is unreasonable. As an example of what electroanalysis is capable of, when there is no restriction on complexity of apparatus or quantity of material to be taken for analysis, reference may be made to a paper on the exact electrolytic assay of refined copper. The results are accurate to 0·01 per cent.[81]

The estimation of the acidity of tan liquors is rendered difficult by their dark colour, which tends to mask the colour change of ordinary indicators. The electrometric method, based on the determination of the difference of potential between the liquid under examination and a plate of platinised platinum saturated with hydrogen, was formerly more or less impracticable owing to

[75] J. Stoddard, *Ann. Report*, 1910, 170; R. C. Benner, *ibid.*

[76] R. C. Benner and L. M. Hartmann, *J. Amer. Chem. Soc.*, 1910, **32**, 1628; *A.*, ii, 148.

[77] R. C. Benner and W. H. Ross, *ibid.*, 1911, **33**, 493, 1106; *A.*, ii, 443, 770.

[78] F. Fisher, C. Thiele, and E. Stecher, *Zeitsch. Elektrochem.*, 1911, **17**, 905 *A.*, ii, 1129.

[79] *Ibid.*, 906; *A.*, ii, 1129.

[80] H. J. S. Sand, *Chem. News*, 1911, **103**, 14.

[81] G. L. Heath, *J. Ind. Eng. Chem.*, 1911, **3**, 74.

complication of apparatus. Recently, however, the apparatus for such purposes has been so much improved for the purpose of the electro-analytical separation of metals [82] that its application is now an exceedingly simple matter, and two important papers on the estimation of the acidity of tan liquors by the electrometric method have been read and discussed within the year. The indications of the electrometric method have a degree of certainty and objectiveness not approached by other methods, but the interpretation of the results in terms of direct value to the tanner is a matter which now needs and merits research.[83]

Organic Analysis.

Few qualitative reactions are sufficiently important to find mention in such a report as this. One depending on the influence of compounds of a certain type on the crystalline form of iodoform is, however, interesting. First described some years ago,[84] and supposed at one time to be specific for aromatic inner anhydrides,[85] it is now known that it is given by aromatic hydroxy-acids with a long side-chain and by polyhydroxy-ketones, but with a slight modification of the original procedure it is said that the reaction may still be accepted as proof of the presence of aromatic inner anhydrides.[86]

A reaction capable of detecting phenol or salicylic acid in a dilution of 1 per million may prove useful on account of its delicacy, but, since it depends on the formation of tri-iodophenol, it is scarcely likely to prove specific.[87]

As regards ultimate analysis, it has been pointed out that cobalt oxide has certain advantages over copper oxide, and that metallic nickel, prepared in a particular way, serves well for the reduction of oxides of nitrogen.[88] A method has also been described for the simultaneous estimation of carbon, hydrogen, oxygen, nitrogen, sulphur, and halogens,[89] whilst a simple and accurate method for the determination of iodine in certain compounds, which yield erratic results when treated by Carius' method, has been based on the fact that the organic matter is completely oxidised when the

[82] H. J. S. Sand, *Trans. Faraday Soc.*, 1909, **5**, 159.

[83] H. J. S. Sand and D. J. Law, *J. Soc. Chem. Ind.*, 1911, **30**, 3; *A.*, ii, 233. J. T. Wood, H. J. S. Sand, and D. J. Law, *ibid.*, 872; *A.*, ii, 942.

[84] B. Bardach, *Chem. Zeit.*, 1909, **33**, 570; *A.*, 1909, ii, 626.

[85] B. Bardach, *Zeitsch. anal. Chem.*, 1911, **50**, 545; *A.*, ii, 826.

[86] B. Bardach, *Chem. Zeit.*, 1911, **35**, 934; *A.*, ii, 945.

[87] J. M. Wilkie, *J. Soc. Chem. Ind.*, 1911, **30**, 402; *A.*, ii, 547.

[88] A. Kurtenacker, *Zeitsch. anal. Chem.*, 1911, **50**, 548; *A.*, ii, 823.

[89] J. A. A. Auzies, *Bull. Soc. chim.*, 1911, [iv], **9**, 815; *A.*, ii, 928

substance is treated with permanganate and nitric acid, the chlorine and bromine being converted into volatile products, whilst the iodine remains as iodic acid.[90] The nitrogen in oximes may be estimated by oxidising these by means of a standard solution of ferric chloride, the excess of which is subsequently determined iodometrically. The results are accurate within 0·05 c.c. of the standard solutions used.[91]

Some years ago Sudborough and Hibbert outlined a general method for the quantitative estimation of amines, based on the measurement of the volume of methane evolved when these substances are caused to react with magnesium methyl iodide.[92] They also employed a similar method for estimating hydroxyl compounds, and obtained satisfactory results in most cases.[93] Zerewitinoff subsequently showed that this method could be used for the most varied types of hydroxy-derivatives, and also for estimating the reactive hydrogen in other groups of compounds, for example, hydrosulphides, imides, and amides.[94] At a later date Sudborough and Hibbert were able to show that their original method was capable of general application, not only for the estimation of primary and secondary amines, but also for the quantitative determination of mixtures of these with tertiary amines.[95] Zerewitinoff, having shown that the method is of service, even in the case of such complicated compounds as sugar and flavone, has now extended it to the alkaloids—derivatives of tertiary amines. These react with magnesium methyl iodide in pyridine solution if they contain hydroxyl groups, and the results at the ordinary temperature are practically identical with those obtained on heating to 85°; this is regarded as evidence that they contain no amino-group, since, as a rule, amino-groups only react with one hydrogen at the ordinary temperature, but on heating the mixture to 85° the second hydrogen atom reacts quantitatively. Certain tautomeric compounds, containing the group $CO{\cdot}CH_2$, which is capable of assuming the form $C(OH){:}CH$, yield results below the theoretical unless the reactions be conducted at a temperature approximating 100°. Similarly, primary and secondary nitro-compounds of the aliphatic series are capable of assuming a pseudo-acid form, in

[90] A. F. Seeker and W. E. Mathewson, *U.S. Dept. of Agric., Bureau of Chem.*, Circular No. 65.

[91] R. Fabinyi, *7th Intern. Congr. Appl. Chem.*, 1909, IV, A1, 171; *A.*, ii, 534.

[92] J. J. Sudborough and H. Hibbert, *Proc.*, 1904, **20**, 165.

[93] J. J. Sudborough and H. Hibbert, *Trans.*, 1904, **85**, 933.

[94] T. Zerewitinoff, *Ber.*, 1907, **40**, 2023; 1908, **41**, 2233; *A.*, 1907, ii, 509; 1908, i, 593.

[95] J. J. Sudborough and H. Hibbert, *Trans.*, 1909, **95**, 477.

which they form salts in virtue of the labile group $R{\cdot}CH{:}N{<}^{O}_{OH}$, which reacts with magnesium methyl iodide. These also give results below the theoretical at the ordinary temperature, and the reaction is not quite complete even at 100°.[96] A recent proposal to use magnesium ethyl iodide and to determine the evolution of ethane by loss of weight,[97] instead of by direct measurement, may prove serviceable in special circumstances, but the original volumetric method owes its importance largely to its rapidity and the fact that only small quantities of substance are required.

Following Fischer and Freudenberg's observations on the properties of carbalkyloxy-derivatives of tannins,[98] Daniel and Nierenstein have based a method for the estimation of hydroxyl groups in substances of the tannin class on the saponification of these derivatives, the preparation of which offers the advantage that intramolecular changes and splitting up of the sensitive tannin compounds are apparently excluded. The saponification takes place according to the equation:

$$R{\cdot}O{\cdot}CO_2R' + H_2O = R{\cdot}OH + CO_2 + R'{\cdot}OH,$$

and the quantitative estimation consists in weighing the carbon dioxide split off.[99]

The reaction of enolic compounds with ferric chloride plays an important part in the study of cases of desmotropy for the detection of the point at which the ketonic form begins to change into the enolic form. By the use of suitable standards and a colorimeter, this reaction may be employed in a quantitative sense for the study of the equilibria at different temperatures and in different solvents. The maximum colour intensity is attained when 1 molecule of ferric chloride reacts with 1 molecule of the enol. A convenient standard is obtained by mixing a solution of the pure enolic form with an equimolecular quantity of dry ferric chloride. This solution is compared with an equally concentrated solution of the enol–ketone mixture to be examined containing the same quantity of ferric chloride as the standard solution. In some cases where the enolic form cannot be obtained in the pure state or is insufficiently stable in solution, standards are prepared from the readily isolated ferric enol salts of the general formula FeR_3, which give maximum colorations when mixed with 2 molecules of ferric chloride and 3 molecules of hydrogen chloride. In certain other cases it is possible to use as standards stable solutions, in which the

[96] T. Zerewitinoff, *Ber.*, 1910, **43**, 3590; *A.*, i, 101.
[97] B. Oddo, *ibid.*, 1911, **44**, 2048; *A.*, ii, 826.
[98] E. Fischer and K. Freudenberg, *Annalen*, 1910, **372**, 32; *A.*, 1910, i, 265.
[99] K. C. R. Daniel and M. Nierenstein, *Ber.*, 1911, **44**, 701; *A.*, i, 371.

equilibrium has been reached and the percentage of enol determined by one of the other standards.[1]

Of the several organic acids of the aromatic series which have been recommended for use as standards in acidimetry, *p*-amino-*o*-sulphobenzoic acid appears to be the most suitable for the purpose. It is a well-defined substance, easily prepared in a pure condition, and as it is anhydrous it can be thoroughly dried in any convenient manner without risk of alteration in composition. The end reaction on titration with phenolphthalein is sharp, and the quantity of sodium hydroxide required for neutralisation coincides so closely with the theoretical quantity as to meet the most exact requirements of volumetric analysis.[2]

The use of titanium trichloride in volumetric analysis first suggested by Knecht and Miss Hibbert for the titration of azo- and nitro-compounds,[3] and referred to in previous reports,[4] has been extended to the estimation of quinones.[5]

A method is now available for the estimation of small quantities of acetic anhydride in acetic acid. It depends on the fact that 2:4-dichloroaniline reacts rapidly with acetic anhydride, but not with acetic acid at the ordinary temperature. The resulting anilide is readily and quantitatively converted into a chloroamine, and the accurate estimation of the latter is extremely easy by reason of its quantitative reaction with hydriodic acid, and the titration of the free iodine with thiosulphate.[6]

When Jörgensen's method for the differentiation of organic plant acids[7] is applied, aconitic acid is estimated partly as citric and partly as malic acid. By the application of a polarimetric method for the estimation of malic acid[8] and by other means,[9] it is now possible to estimate aconitic acid with some approach to accuracy, even in admixture with many other vegetable acids. One of the first results of the application of the new method is the proof that aconitic acid is the preponderant acid in sugar-cane juice.

In 1905, Steinegger[10] showed that the protein content of milk

[1] L. Knorr and H. Schubert, *Ber.*, 1911, **44**, 2772; *A.*, i, 948.
[2] J. H. Kastle, *Amer. Chem. J.*, 1910, **44**, 487; *A.*, ii, 66.
[3] E. Knecht and Miss E. Hibbert, *Ber.*, 1903, **36**, 1549; *A.*, 1903, ii, 509.
[4] *Ann. Report*, 1905, 195; 1907, 211.
[5] E. Knecht and Miss E. Hibbert, *Ber.*, 1910, **43**, 3455; *A.*, ii, 76.
[6] Miss M. G. Edwards and K. J. P. Orton, *Trans.*, 1911, **99**, 1181.
[7] G. Jörgensen, *Zeitsch. Nahr. Genussm.*, 1907, **13**, 241; *A.*, 1907, ii, 312.
[8] P. A. Yoder, *J. Ind. Eng. Chem.*, 1911, **3**, 563; also *Zeitsch. Nahr. Genussm*, 1911, **22**, 329; *A.*, ii, 1141.
[9] P. A. Yoder, *J. Ind. Eng. Chem.*, 1911, **3**, 640.
[10] R. Steinegger, *Zeitsch. Nahr. Genussm.*, 1905, **10**, 659; *A.*, 1906, ii, 130.

was approximately proportional to the values obtained by neutralising the milk, adding excess of formaldehyde, and then titrating the now acid solution with alkali hydroxide. He appeared to have no knowledge of the work of Schiff [11] on discrimination between basic and acidic functions in solutions of amino-acids and proteins, and he termed his titration values the "aldehyde figure" of the milk, although he was not measuring aldehyde, nor measuring anything else in terms of formaldehyde, but simply using the latter to annul the basic function of the protein molecules so that their carboxyl groups could be titrated. It is now known that Schiff's reaction is reversible, but means have been found to make the end-point of the titration such that the hydrion concentration is as low as $10^{-9\cdot7}$, under which conditions the reaction is approximately quantitative,[12] and the method has been widely applied in connexion with physiological work.[13] As applied to the estimation of proteins in milk, it is now shown that the method gives results of the same order of accuracy as the centrifugal methods for the estimation of fat.[14] With rare abnormal samples the error is considerable, and with milk in which bacterial or enzymic action has proceeded far it must necessarily give results above the truth if the factor for normal milk proteins be applied. Unfortunately, the titration values continue to be called the "aldehyde figure," an expression which is perplexing to many when they first encounter it, whereas "amino-acid number" would be readily intelligible, and would also suggest the limitations of the method. The cryoscopic method for the detection of added water in milk [15] has been applied to some 2500 French samples, and the author concludes that the method will distinguish between genuine and watered milks, notwithstanding differences of age, provided a suitable correction, given in the paper, be made for the lactic acid present. A freezing point above $-0\cdot530°$ is said to be conclusive evidence of watering, whereas a normal freezing point of $-0\cdot550°$ should be accepted as proof of genuineness whatever be the results of chemical analysis.[16]

The methods of Ewers and Fendler for the detection of cocoanut oil in butter, referred to in last year's report [17] as likely to prove useful, have scarcely fulfilled that expectation,[18] and the Polenske method remains the only chemical method by which small quanti-

[11] H. Schiff, *Annalen*, 1902, **319**, 59, 287; **325**, 348; *A.*, 1902, i, 85, 250; 1903, i, 232.

[12] *Ann. Report*, 1908, 205.

[13] *Ibid.*, 1910, 181.

[14] H. D. Richmond, *Analyst*, 1911, **36**, 9; *A.*, ii, 236.

[15] W. R. G. Atkins, *Chem. News*, 1908, **97**, 241; *A.*, 1908, ii, 641.

[16] L. Stoecklin, *Ann. Falsif.*, 1911, **4**, 232.

[17] *Ann. Report*, 1910, 177.

[18] E. Nockmann, *Zeitsch. Nahr. Genussm.*, 1911, **21**, 754; A. Hepner, *ibid.*, 758.

ties of cocoanut oil can be detected and approximately estimated in butter. Its alleged failure in certain cases can usually be traced to a disregard to experimental details which are of the essence of the process. Kirschner's extension [19] of the Reichert-Meissl process offers little value over the Polenske method for cocoanut oil in butter, but, as the result of an exhaustive research on the subject, the opinion has been expressed that it is the only published method at present available which will decide whether butter-fat is present in a margarine containing cocoanut oil, even if the amount be only 2 per cent. in conjunction with 75 per cent. or more of cocoanut oil.[20]

The utility of Fiehe's test [21] for the detection of artificial invert sugar in honey, which depends on the presence of α-hydroxy-δ-methylfurfuraldehyde in all artificial invert sugar, continues to find confirmation,[22] and a simplified procedure using a different reagent from that employed by Fiehe has been described.[23] Reactions characteristic of natural honey are of little value for the detection of adulteration unless they can be made quantitative and some "standard" agreed on as representing genuine honey. These conditions appear to be fulfilled in the case of Langer's interesting serological test,[24] which can be made roughly quantitative, whilst the quantitative results yielded by the genuine honeys so far examined lie very close together.[25]

The estimation of nicotine received an unusual amount of attention during 1911. Tobacco extracts are now an important article of commerce, and the prices of competing brands only differ by about 10 per cent. from the mean price, whilst the percentage of nicotine may be anything from 1·5 to 11 per cent.[26] In the interest alike of purchasers and of the more reputable manufacturers, the introduction of the unit system of payment seems desirable. This implies, however, the existence of one or more accurate methods for the estimation of nicotine, or, failing such, an international agreement as to the manner in which nicotine is to be estimated. Early in the year the latter course was recommended as the result of experiments which showed that existing methods gave very

[19] Kirschner, *Zeitsch. Nahr. Genussm.*, 1905, **9**, 65; *A.*, 1905, ii, 213.
[20] C. Revis and E. R. Bolton, *Analyst*, 1911, **36**, 333.
[21] J. Fiehe, *Ann. Report*, 1910, 174.
[22] G. Curtel, F. Muttelet, and E. Moreau, *Ann. Falsif.*, 1910, **3**, 497, 503, 513; W. Hartmann, *Zeitsch. Nahr. Genussm.*, 1911, **21**, 374; H. Luhrig and A. Scholz, *ibid.*, 721.
[23] E. Feder, *Zeitsch. Nahr. Genussm.*, 1911, **21**, 412.
[24] J. Langer, *Ann. Report*, 1910, 174.
[25] J. Thöni, *Mitt. Lebensmittelunters. u. Hyg.*, 1911, **2**, 80.
[26] J. Schröder, *Zeitsch. anal. Chem.*, 1911, **50**, 433.

variable results.[27] The immediate result of this proposal was a crop of papers in defence of old methods and descriptive of new ones, and withal so hostile to yet other old ones that for a time confusion was rendered worse confounded. The net result, however, appears to be that there is no necessity for the imposition of any one method—always an undesirable proceeding when commercial interests can be served without resort to it. In a recent paper Tóth has shown that his method, into which he has introduced modifications,[28] Kissling's method among the older ones, and a new polarimetric method due to Degrazia,[29] yield substantially identical results, provided the extract under examination has not been sophisticated by addition of pyridine bases. In their presence Kissling's method over-estimates nicotine. The simple method of Ulex is said by many authors to give unduly high results, but there is some doubt whether it has had a fair trial. Although the principle of the method has been made use of in many laboratories for years, and has rightly been attributed to Ulex, it appears that that author never himself published the details of his method until the recent controversy.[30]

In the absence of any other good method for the determination of codeine in opium, a new volumetric method which appears to be accurate is worthy of reference.[31] Nishi's method[32] for the estimation of quinine in organic liquids, such as urine, has been simplified, and found to yield excellent results. It does not distinguish between quinine and the other common cinchona alkaloids, but may be employed for the estimation of quinine in presence of caffeine.[33] In competition for the Hagen-Bucholz prizes of the Deutscher Apotheker Verein, A. Kneip, N. Ney, and F. Reimers each investigated some twenty methods for the estimation of cantharidin in cantharides and its tincture. Only one of the competitors recommends a method which can be described as new, but their results are valuable, and rendered more so by the fact that they are presented together in a single critical memoir by Emde.[34]

Since the value of turpentine in practice depends on the rapidity with which it absorbs oxygen, some interest attaches to a recent paper, in which it is proposed to determine the relative value of different samples from this point of view, the method described

[27] J. Schröder, *Chem. Zeit.*, 1911, **35**, 30; *A.*, ii, 163.
[28] J. Tóth, *ibid.*, 926; *A.*, ii, 943.
[29] J. von Degrazia, *Fach. Mitt. österr. Tabakregie*, 1910, 149; *A.*, ii, 671.
[30] H. Ulex, *Chem. Zeit.*, 1911, **35**, 121; *A.*, ii, 344.
[31] A. E. Andrews, *Analyst*, 1911, **36**, 489; *A.*, ii, 1144.
[32] M. Nishi, *Arch. exp. Path. Pharm.*, 1909, **60**, 312; *A.*, 1910, ii, 710.
[33] T. Cockburn and J. W. Black, *Analyst*, 1911, **36**, 396; *A.*, ii, 944.
[34] H. Emde, *Arch. Pharm.*, 1911, **249**, 259; *A.*, ii, 669.

depending on the oxidation of cymyl mercaptan by the peroxide formed in the turpentine.[35]

The large number of abstracts appearing in this year's Journal on the direct estimation of caoutchouc in raw rubber by chemical methods may lead to the expectation of a somewhat extended paragraph on the subject in this report, but in the writer's opinion it is too early yet to attempt to collate the results obtained, which in the present state of our knowledge appear irreconcilable. By far the greater number of papers are concerned with modifications of the tetrabromide method,[36] and this may perhaps be taken as evidence that a majority of those most interested think that the solution of the problem is most likely to be found in this direction. In support of this view are the facts that the composition of the tetrabromide is beyond question, and that it is sufficiently insoluble to serve as the basis of an analytical process. On the other hand, the conflicting results obtained by different workers under conditions supposed to be identical show that the conditions essential for the quantitative conversion of caoutchouc into the tetrabromide have yet to be determined. In these circumstances the proposal to extend the use of the method to vulcanised articles seems premature, and it has been shown that it may lead to ridiculous results.[37] The nitrosite method [38] finds fewer critics, but few supporters. One modification of it may be noted,[39] as it is said to give results in close agreement with those yielded by the method, much in use, according to which caoutchouc is estimated by evaporation of the filtered solution of the resin-free rubber. There is doubt, however, whether the so-called "nitrosite" has the composition assigned to it by Harries, and some evidence that the results obtained by the method depend for their accuracy on a compensation of errors.[40]

The valuation of crude glycerol has in recent years assumed greater commercial importance owing to the increased value of the commodity. The want of uniformity in the methods of analysis, together with the irregularity of the results obtained, emphasised the desirability for the standardisation of crude glycerol analysis, and with this object in view committees were formed in America, France, Germany, and Great Britain. These committees worked in the first place independently, but were ultimately brought together, and after a series of conferences a unanimous report was

[35] P. Klason, *Chem. Zeit.*, 1911, **35**, 537 ; *A.*, ii, 665.
[36] T. Budde, *Ann. Report*, 1907, 214.
[37] W. Esch, *Chem. Zeit.*, 1911, **35**, 971 ; *A.*, ii, 946.
[38] P. Alexander, *Ann. Report*, 1907, 214.
[39] O. Korneck, *Gummi-Zeit.*, 1910, **25**, 4, 42, 77 *A.*, ii, 545.
[40] P. Alexander, *Zeitsch. angew. Chem.*, 1911, **24**, 680 ; *A.*, i, 389.

agreed on. The methods detailed in this report are strongly recommended as International Standards.[41]

Agricultural Analysis.

A paper which shows that the unavoidable error in sampling soils is of the order of 5 per cent.,[42] somewhat discounts the value of refined analytical methods in soil analysis. In one determination, however, namely, that of humus, the uncertainty of the analytical results has hitherto been far greater than this, and it is gratifying to be able to record the fact that a simple method has now been devised which reduces this uncertainty to very small dimensions.[43]

The products of the new processes for the fixation of atmospheric nitrogen having now reached the markets in considerable quantities, means for their accurate analysis assume some importance, and the past year has witnessed the appearance of a number of papers which, read together, appear to place this subject on a fairly satisfactory footing, although there is not yet that exact accord between authors which commercial interests might wish to see established. The analysis of calcium cyanamide, which appears in commerce in two distinct forms, distinguished in Germany by the names "Stickstoffkalk" and "Kalkstickstoff" (the former containing calcium chloride), has necessarily engaged the attention of Caro and his collaborators. They have worked out a method for the separate estimation of dicyanodiamide and carbamide, present in small quantity in all commercial samples of calcium cyanamide and in larger quantity in samples which have been long stored, and they show that the cyanamide can be estimated accurately by precipitation with an ammoniacal solution of silver acetate and determination of the nitrogen in the washed precipitate by Kjeldahl's method. The precipitate contains an amount of silver which varies with the conditions of the precipitation, but the whole of the cyanamide is thrown down.[44] The statement of Kappen[45] that it is easy to secure a precipitate having the composition represented by the formula $CN{\cdot}NAg_2$, must be received with caution, as, although his figures show that his precipitates closely approximated this composition, his general statement conflicts, not only with that of Caro, but with that of at least two other authors.[46, 47]

[41] Hehner and others, *Analyst*, 1911, **36**, 314.
[42] E. A. Mitscherlich and E. Merres, *Landw. Jahrb.*, 1910, **39**, 345; *A.*, ii, 68.
[43] J. B. Rather, *J. Ind. Eng. Chem.*, 1911, **3**, 660.
[44] N. Caro and others, *Zeitsch. angew. Chem.*, 1910, **23**, 2407; *A.*, i, 119.
[45] H. Kappen, *Chem. Zeit.*, 1911, **35**, 950; *A.*, ii, 933.
[46] R. Monnier, *ibid.*, 601; *A.*, ii, 668. [47] A. Stutzer, *ibid.*, 694; *A.*, ii, 777.

Kappen makes use of a slight modification of the first method[48] ever proposed for the estimation of cyanamide, and, after what has been said, reference must be given to his first and detailed description of it.[49] In principle it depends on the precipitation of cyanamide by a measured excess of an ammoniacal solution of silver nitrate of known strength, and titration of the excess of silver by means of thiocyanate. A statement has been repeated in many journals to the effect that Caro's method fails to estimate the whole of the cyanamide, and that this failure appears to be due to silver cyanamide being insufficiently insoluble to afford an accurate basis on which to found an analytical process. An examination of the original paper[50] in which the statement was first made shows, however, that its author, although he quotes Caro, did not use the latter's method, but determined the silver instead of the nitrogen in the precipitate.

Of more importance, perhaps, from a commercial point of view, is the estimation of the total nitrogen in these new fertilisers. It might be expected that this would present no special difficulty, but a survey of the literature affords evidence to the contrary. It has been variously stated that commercial calcium cyanamide does not yield all its nitrogen as ammonia when subjected to the Kjeldahl process unless salicylic acid and zinc dust or other reducing substance are present,[51] that the unmodified Kjeldahl process gives accurate results,[52] and that neither process yields the whole of the nitrogen as ammonia. At the date of this report the last word rests with an author who adduces strong evidence to show that accurate results may be obtained by the use of sulphuric acid diluted with an equal bulk of water.[53]

The analysis of Norwegian nitre, which is essentially a mixture of calcium nitrate and hydroxide, with a variable but never negligible proportion of nitrite, presents fewer difficulties. Difficulty was formerly experienced in determining the moisture content, but this has been overcome in a simple manner.[54] The estimation of nitrite presents no difficulty, and the total nitrogen is readily estimated by reduction to ammonia by means of "Devarda metal," or may be determined by means of "nitron" after oxidation of the nitrite by permanganate. Experiments have shown that oxidation of the nitrite by means of hydrogen peroxide is never quantitative, nor is it practicable to attempt the decom-

[48] R. Perotti, *Gazzetta*, 1905, **35**, ii, 228; *A.*, 1905, ii, 870.
[49] H. Kappen, *Landw. Versuchs.-Stat.*, 1909, **70**, 445; *A.*, 1909, ii, 609.
[50] R. Monnier, *loc. cit.*
[51] *Ibid.*, *loc. cit.* [52] Stutzer, *loc. cit.*, and Kappen, *loc. cit.*
[53] E. Dinslage, *Chem. Zeit.*, 1911, **35**, 1045; *A.*, ii, 1027.
[54] Dinslage, *loc. cit.*

position of the nitrite by means of hydrazine sulphate as a preliminary to a direct determination of nitrate, as such decomposition is never complete.[55] The latter observations have significance beyond the narrow limits of the subject under which the paper is indexed.

Physiological.

Van Slyke has further developed his modification of the Sachsse-Kormann method for the estimation of aliphatic amino-groups,[56] and his more recent papers[57] are so detailed as to be intelligible when read alone without reference to the earlier literature of the subject. Every known amino-acid reacts quantitatively with one, and only one, nitrogen atom, except lysine, which reacts with two, and proline and oxyproline, which do not react at all. On this last fact has been founded an accurate method for the estimation of proline in admixture with other amino-acids.[58] The fact that the copper salts of amino-acids separate copper hydroxide on boiling with alkali, whilst the copper compounds of peptones and peptides are not decomposed on such treatment, may be made to serve for the detection of amino-acids among the products of protein hydrolysis, and for the study of the quantitative relationships which exist between the nitrogenous substances of greater or less complexity at successive stages in an experiment with proteoclastic enzymes.[59] The use of triketohydrindene hydrate for the detection of proteins and their derivatives[60] has been further investigated. The reagent gives a blue coloration with α-amino-acids, polypeptides, peptones, and proteins, with certain exceptions, which suggest that the reaction is characteristic of compounds which have both a free amino-group and a free carboxyl group. The reaction is one of great sensitiveness, glycine and alanine being detectable by means of it even in dilutions of 1 : 10,000.[61]

The writer of the last annual report made complaint of the unnecessary multiplication of analytical methods by physiologists,[62] and the last year affords a striking instance of this. Of the so-called methods for the detection of adrenaline,[63] those depending on the colour developed on treatment with iodine, mercuric chloride, and

[55] A. Stutzer and Goy, *Chem. Zeit.*, 1911, **35**, 891 ; *A.*, ii, 933.
[56] *Ann. Report*, 1910, 181.
[57] D. D. van Slyke, *J. Biol. Chem.*, 1911, **9**, 185 ; **10**, 15 ; *A.*, ii, 779, 944.
[58] *Ibid.*, 205 ; *A.*, ii, 780.
[59] P. A. Kober, *ibid.*, 1911, **10**, 9 ; *A.*, i, 824.
[60] S. Ruhemann, *Trans.*, 1910, **97**, 2025.
[61] E. Abderhalden and H. Schmidt, *Zeitsch. physiol. Chem.*, 1911, **72**, 37 ; *A.*, ii, 674.
[62] *Ann. Report*, 1910, 157.
[63] *Ibid.*, 1909, 155.

iodic acid respectively have been shown to be substantially identical, that is to say, the reagent in each case acts as oxidising agent. A new reaction, said to be somewhat more sensitive than those previously described, depends on the use of potassium persulphate, and the reaction in this case is known to be one of oxidation.[64] It is to be noted that several of the other reagents, suggested from time to time for the detection of adrenaline, are capable of functioning as oxidisers, but whether this is their rôle in the adrenaline test remains to be determined. Nearly all these colour reactions are given by other closely related compounds, and although it is claimed for some that they are specific, such claims must be received with caution. Now that it is known that many of them depend on oxidation, systematic experiment with more or less powerful oxidising agents might result in making the test more specific at some expense of sensitiveness, as has been done with the methods for the detection of methyl alcohol in presence of ethyl alcohol by oxidation of the former to formaldehyde.

It has been found that the presence of hæmoglobin in urine cannot be detected by means of the absorption spectrum unless the urine is quite fresh, and there is some evidence that this is due to destruction of the hæmoglobin by hippuric acid. Whether or no this is the true explanation of the disappearance of the characteristic absorption bands, the research has led to the observation that by the simple expedient of adding a slight excess of ammonia to a sample of urine immediately after collection, it may be preserved for a reasonable time in a state fit for spectroscopic examination.[65] For the direct estimation of creatine in pathological urine, a method has been described which depends on the fact that diacetyl reacts with creatine, but not with creatinine.[66] The determination of lecithin should be rendered more certain by the work of Cohn, who has investigated the conditions governing the extraction of lecithin from substances containing it.[67]

In another section of this report attention has been called to the use of a serological method for the identification of honey, and for its approximate estimation in admixture with other substances. By the intravenous injection of ricin into rabbits, an anti-ricin serum has been prepared which serves as a precipitation reagent for the detection of the poisonous constituents of castor seeds in cattle foods,[68] and a method dependent on the same principle has been used for identifying various kinds of flesh, for example, horse-

[64] A. J. Ewins, *J. Physiol.*, 1910, **40**, 316 ; *A.*, 1910, ii, 557.
[65] F. A. McDermott, *J. Amer. Chem. Soc.*, 1911, **33**, 992 ; *A.*, ii, 674.
[66] G. S. Walpole, *J. Physiol.*, 1911, **42**, 301 ; *A.*, ii, 671.
[67] R. Cohn, *Zeitsch. öffentl. Chem.*, 1911, **17**, 203 ; *A.*, ii, 779.
[68] W. Mooser, *Landw. Versuchs-Stat.*, 1911, **75**, 107.

flesh in sausages.[69] Certain antiseptics, such as sulphites and formaldehydes, interfere with the latter test, but the interest attaching to these tests depends less on their intrinsic value, although that may prove considerable, than on the expectation they raise that analytical chemistry will in the near future make more extended use of similar methods.

G. Cecil Jones.

[69] A. Saint-Sernin, *Ann. Falsif.*, 1911, **4**, 334.

PHYSIOLOGICAL CHEMISTRY.

The year 1911, so far as Physiological Chemistry is concerned, has been one of quiet, uninterrupted progress, but it cannot be described as an eventful year. There is no great discovery to be chronicled, and no research or series of researches stands out conspicuously among its fellows.

Amongst those who have passed away, one must specially mention the names of Dr. Pavy and Professor Christian Bohr.

Dr. Pavy was one of those few indefatigable spirits who, like Dr. Ringer, whose loss we had to deplore last year, was able to carry out important scientific work in the midst of a life of busy medical practice. He is best known as the redoubtable opponent of Claude Bernard's views on carbohydrate metabolism, and he continued almost up to the day of his death, at the ripe age of eighty-four, to work at the subject he had made his own. In the last few years he became interested in the part played by the colourless corpuscles of the blood in the transport of substances absorbed from the intestine, and his last paper,[1] published posthumously, deals with the power these corpuscles have in incorporating dextrose in their protoplasm. Pavy's familiar figure will be much missed in medical and physiological circles, and the world will be the poorer by his absence.

One little thought last year when penning the section of the report dealing with the subject of respiration, that it would be necessary twelve months later to deplore the loss of Christian Bohr, of Copenhagen, the leader and inspirer of those researches which have culminated in our present knowledge of the processes involved in breathing. Although all of Bohr's deductions from his experiments have not been universally accepted, especially in relation to the part played by the so-called "vital factor," it cannot be denied that it was the boldness and novelty of his conceptions that led others to take up the subject afresh, and test them by further experiment. Unlike Pavy, Bohr was a comparatively young man, and his being

[1] F. W. Pavy and W. Godden, "Carbohydrate Metabolism and Glycosuria," *J. Physiol.*, 1911, **43**, 199; *A.*, ii, 1001.

suddenly cut off in his prime adds exceptional sadness to the regret at his death which is so universally felt.

The year has been singularly destitute of chemical or physiological Congresses. The British Association and the British Medical Association have had their usual annual meetings with their physiological sections. In the case of the latter body, physiology was combined with anatomy in one section, and the major part of the papers read were anatomical. The Portsmouth meeting of the British Association for the Advancement of Science was a comparatively small one, but was not less interesting on that account. It, in fact, often happens that interest and fullness of attendance are in inverse proportion. This was certainly the case with the section of Physiology, which was opened by a highly speculative address by the President, Professor Macdonald, and was followed by a number of well-sustained discussions on important subjects. The section of Chemistry also was notable for the address of its President, Professor James Walker, on the history of Physical Chemistry, which is now so intimately associated with the latter-day developments of physiology.

The foundation of the Bio-chemical Club in London during the year is an indication that bio-chemists are realising, not only their strength, but also the importance of union, which forms so large an element in strength. Its meetings hitherto have been highly successful, and are combinations of scientific discussion with the more social intercourse which accompanies and follows the eating of dinners. The Club is looking forward with hopefulness to a not-distant future when it will develop into a Society with a journal of its own.

Among the new books of the year it is necessary to mention a text-book of comparative physiology by Professor Pütter.[2] This is not of the same ambitious character as that edited by Winterstein, to which allusion was made in last year's Report, but it is nevertheless a comprehensive treatise, and not too bulky. In the investigation of the lower, as well as of the higher, animals, chemistry is playing a conspicuous part, and in Professor Pütter's book special prominence is assigned to the rôle of physical chemistry in the elucidation of vital problems.

Another book which may be read with interest and profit is entitled, "Chemical Phenomena in Life," and its author is Professor Frederick Czapek,[3] of Prague. It only extends over 148 small pages, but the amount of information packed within this small compass is really remarkable. There is no indication of undue

[2] "Vergleichende Physiologie." A. Pütter. Fischer; Jena, 1911.

[3] Harper's "Library of Living Thought," 1911.

compression; the facts are stated in a clear, convincing, and comprehensible style. Professor Czapek is a botanist, but he deals with his subject from the point of view of general biology. He shows how many of the phenomena of life are rendered intelligible in the light of colloid chemistry, and by the conception of enzymes as organic catalysts. The same subject may, of course, be studied in larger and more elaborate treatises, but to those who are not physical chemists, a little book of this nature is a veritable godsend; it gives in outline the main facts, the new ideas, and explains in simple terms the new language which has been introduced into science by the physical chemists.

Periodical literature, as I have already indicated in my opening sentence, remains quite as voluminous as in former years. To sift the chaff from the wheat is not possible at present. That only can be performed by the reviewer of the future. Many pieces of original work which appear valueless at the time of publication often turn out to be of exceptional importance, and the converse is equally true. It is also impossible to attempt, even in outline, a survey of the whole output of the year or to classify it. The published papers deal with practically every branch of the subject. The only remaining alternative is to follow my custom of previous years, and make a selection, which I trust will be found a judicious one.

I propose, then, in the first place, to deal with one or two points of nomenclature; next, rapidly to review a certain number of papers which appear in my judgment to be of exceptional interest, and, finally, to select for rather more extended notice a few of the topics which are attracting attention at the present day. In this preliminary stage of my essay it is impossible to forecast with certainty what these topics will be, but at this point my intention is to deal with three only: first, the enzymes concerned in nuclein metabolism, a somewhat specialised and technical albeit important subject; secondly, the vexed questions which have centred around "Standard Bread," a subject of interest even to the man in the street; and the third subject will be a pathological one, namely, the causation of that tropical disease which is named "beri-beri."

Some Questions of Nomenclature.

The terminology of enzymes has settled down in the majority of cases to the following rule. They are usually named after the substances they split up, and end in the affix *ase*; for instance, maltase is the name for the enzyme which decomposes maltose into the smaller

molecules of dextrose, lipase for a fat-splitting enzyme, and so forth. In many cases the reaction is a reversible one, and the same agent which produces the decomposition under certain conditions, will under certain other conditions produce a synthesis of the simpler into the more complex material. The main condition which influences the result is, as is well known, the law of the influence of mass action. Hans Euler and S. Kullberg [4] have, however, pointed out that in certain cases, at any rate, one enzyme is employed in the cleavage, and another enzyme comes into play in the synthetic act. They could find no evidence that the enzyme which builds up phosphoric acid esters of carbohydrates, and which is found in yeast and other moulds, has any action at all in splitting up these esters into their component parts. Euler [5] suggests that in such cases the termination *ese* should be adopted instead of *ase*, and consequently speaks of the enzyme in the example just quoted as *phosphatese*. Another instance where such a system of terminology would be useful is what E. S. London [6] entitles, "A reversible phenomenon in the action of intestinal juice on the products of casein digestion"; at a certain stage the milk protein undergoes jellying, and the subsequent liquefaction is apparently the result of the action of a different enzyme.

Life, so far as its chemical activities are concerned, has recently been defined as consisting of a series of reversible reactions. This is probably as correct a definition of vital metabolism as is possible in the present state of knowledge, but like all terse attempts to compress within a very small nutshell a very complex problem, it lacks completeness, and allows of no exceptions, which are doubtless plentiful.

Be that as it may, reversibility is observable in living structures in cases which permit of no obvious chemical explanation. In the realm of psychology, the only region in which, according to Czapek in the book already mentioned, physico-chemical laws are not at present applicable, a change of mind and a recantation of views are not entirely unknown. Coming, however, to more matter of fact phenomena, Sherrington has furnished many instances where reversal of normal nerve action may be brought about under the influence of certain drugs, for example, chloroform. These are not limited to blood-pressure effects which he had studied in his earlier work, but may occur also in reflexes carried out by skeletal muscles.[7] Another example is furnished by the investigation carried out by

[4] *Zeitsch. physiol. Chem.*, 1911, **74**, 15; *A.*, i, 1051.

[5] *Ibid.*, 13; *A.*, i, 1051.

[6] *Ibid.*, 301; *A.*, ii, 1000.

[7] C. S. Sherrington and Miss S. C. M. Sowton, *J. Physiol.*, 1911, **42**, 383; *A.*, ii, 753; see also Owen and Sherrington, "Strychnine Reversal," *ibid.*, **43**, 232.

Dale and Laidlaw[8]; they found that cytisine, the alkaloid of laburnum seeds, has an action similar to that of nicotine in lessening or reversing the usual effect of stimulation of the chorda tympani nerve in producing an increased flow of saliva.

Another aphorism a good deal older than the one quoted a few paragraphs back, is that language was given to man in order to conceal his thoughts. One cannot help thinking of this when dealing with the second case I take under the heading nomenclature; I mean the introduction of the appalling word *aporrhegma*; thus among this year's Abstracts I find the title, "β-Alanine as a Bacterial Aporrhegma."[9] The word was first introduced a year or two ago, but would be better expunged from the literature. The meaning of the word is a substance split off by biological action.

Another new and useful word is *acapnia*, which has been introduced by Dr. Yandell Henderson, and is gaining acceptance. Carbon dioxide has in the past been looked upon chiefly as a waste product, and of but little use to the organism. We now know that carbon dioxide fulfils *inter alia* the useful office of being the normal stimulus to the respiratory centre, and it assists in the dissociation of oxy-hæmoglobin in the capillaries. If, owing to forced and exaggerated respiratory efforts, this gas is swept out of the blood so that its quantity is reduced below a certain "threshold," the respiratory centre is no longer thrown into action, and cessation of breathing (apnœa) is the result. In normal circumstances, when the carbon dioxide again accumulates, respiration sets in once more. There are, however, certain conditions in which a lessening of the carbon dioxide content in the blood may produce a cessation of breathing, which is serious or even fatal. Notable among these conditions is that produced by surgical and other forms of "shock." Henderson has worked out this aspect of the question in a series of researches, and has bestowed the term "acapnia" to the diminution of the carbon dioxide, which is the cause of the symptoms. The latest of this series[10] appeared about the middle of the year, and in this it is pointed out that acapnia is a frequent concomitant of the glycosuric state, and that in certain forms of experimental diabetes, prevention of acapnia obviates disturbances of the sugar-regulating functions. As long ago as 1889, Labousse pointed out that injection of "peptone" causes acapnia, although he did not employ that expression; it is now found that this also leads to

[8] *J. Physiol.*, 1911, **43**, 196; *A.*, ii, 997.

[9] D. Ackermann, *Zeitsch. Biol.*, 1911, **56**, 87; *A.*, ii, 757.

[10] "Acapnia and Glycosuria," Y. Henderson and F. P. Underhill, *Amer. J. Physiol.*, 1911, **28**, 275; *A.*, ii, 813.

hyperglycæmia. It is often a long time before physiological discoveries filter through to the rank and file of medical practitioners, but one is rejoiced to hear that practical physicians are already appreciating the value of Henderson's work, and are thus beginning to realise, not only the importance of carbon dioxide in the body, but also the meaning of symptoms which previously puzzled them.

A mention of diabetes prompts one at this point to allude by way of parenthesis to an important paper by F. P. Underhill and M. S. Fine[11] on pancreatic diabetes. The hypothesis they advance can only be fully understood by studying the paper in full, a task that will amply repay the reader. The underlying assumption is that there exists between the liver, pancreas, and adrenal bodies an inter-relation which keeps the amount of blood sugar constant. The action of the internal secretion of the pancreas is to facilitate carbohydrate katabolism; therefore, when the pancreas is removed or its function is in abeyance, sugar accumulates, because the opposing effect of the adrenals has full sway. On the other hand, if adrenal function is in abeyance, the deleterious effects of depancreatisation are lessened; they find that hydrazine prevents the glycosuria which occurs after extirpation of the pancreas, in all probability because this drug diminishes adrenal activity.

Pnein and *antipnein* are illustrations of names of unknown substances which are derived from their physiological action. Pnein or pneumin is a thermostable material found, according to Battelli and Stern,[12] in most tissues which accelerate their primary respiration processes. Antipnein or antipneumin is destroyed by a temperature of 65°; it is specially abundant in the spleen, and almost absent in muscle. Its name indicates that it inhibits or hinders oxidative processes. Whether such terms "catch on" and live depends on many circumstances. Many words become familiarised by long usage before their chemical composition is worked out, and so the old names stand. There is little doubt, for instance, that adrenaline and secretin are destined for a long life. Peptone and protagon are still used, although they can no longer be regarded as connoting chemical individuals. The prolonged existence of Popielski's vaso-dilatin appears more questionable, and the continued use of the word "ptomaine" also appears undesirable. The history of our knowledge of the bases obtainable from proteins is a very interesting one.[13] Many of them can be obtained by simply removing carbon dioxide from amino-acids, and one of the latest of these obtained in this way from histidine is 4-*p*-aminoethylgly-

[11] *J. Biol. Chem.*, 1911, **10**, 271; *A.*, ii, 1001.

[12] *Biochem. Zeitsch.*, 1911, **33**, 315; **36**, 114; *A.*, ii, 748, 1008.

[13] See article by G. Barger, *Science Progress*, 1911, p. 221.

oxaline or β-iminazolylethylamine.[14] This is a constituent of ergot, of the intestinal mucous membrane, and is probably identical with Popielski's vaso-dilatin. Its effects are also similar to those which are produced by a toxic substance formed in an anaphylactic animal by the injection of an innocuous protein.

However desirable it may be for sentimental or historical reasons to retain words which have become familiar, there can be no doubt whatever that words framed on chemical misconceptions ought to be ruthlessly expunged. Such a word, for instance, is "quadriurate." Rosenheim [15] was the first to prove that these substances, originally described by the late Sir William Roberts, are mixtures of biurates and uric acid. This view has been repeated and confirmed by R. Kohler [16] during the present year, who was unacquainted with Rosenheim's work. W. E. Ringer [17] has also investigated the same question, and although he lends no support to the chemical entity of these substances, suggests that the peculiar behaviour of uratic deposits in urine, which originally led Sir W. Roberts to his view that uric acid and a biurate were united chemically, can be best explained on the view that this is a case of "solid solution."

Another case of nomenclature, and the last on my list, is that of caseinogen and casein. It was in the year 1890 [18] that I proposed these names for the principal proteins in milk and cheese respectively, as previous to that time the single word casein was usually applied to both indiscriminately, and this led to confusion. The words certainly possess the merit of conveying to the mind easily the relationship of the two substances to one another, and this is by no means unimportant, especially to those who have to deal with students. The terms were obviously suggested by the somewhat similar genetic relationship between fibrinogen and fibrin, and the analogy still holds, although it may not be complete in every detail. They have been very generally adopted by those who write in the English tongue, but those who write in German continue to employ the word "casein" for the milk protein, and the word "paracasein" for the curdled product.[19] In view of this international difficulty,

[14] Barger and Dale, *J. Physiol.*, 1911, **41**, 499; Dale and Laidlaw, *ibid.*, **43**, 182; *A.*, i, 217, 1017. See also, in this connexion, W. H. Harvey, *J. Path. Bact.*, 1911, **16**, 95; *A.*, ii, 1013, on the part played by such bases in the production of kidney disease; and in the causation of high blood pressure, see Bain, *Lancet*, 1911, i, 1409; *A.*, ii, 631.

[15] Rosenheim and Tunnicliffe, *Lancet*, June 16th, 1900.

[16] *Zeitsch. physiol. Chem.*, 1911, **70**, 360; *A.*, i, 243. See also Rosenheim, *ibid.*, **71**, 272; *A.*, i, 403.

[17] *Ibid.*, **75**, 13, *A.*, i, 1044.

[18] *J. Physiol.*, 1900, **11**, 448.

[19] Recent interesting work on milk curdling, especially on the changes in the protein antecedent to actual curdling, and amplifying Hammarsten's classical work

I recently put the question to our newly-founded Bio-chemical Club whether it would be wise to surrender the use of the words caseinogen and casein in favour of the German system, and I was glad to find almost complete unanimity in favour of my own terms. They will therefore continue to live on, and if the Germans do not fall into line, no one need suffer, except perhaps the German students, who will continue to wonder why the protein of milk should be called cheese, and why the protein of cheese is called something else.

Miscellaneous Papers of Interest.

I now come to the second item on my programme, namely, brief notices of various papers which appear to me important ones. Finding it difficult to arrange them in any logical order, I propose to take them almost haphazard, and will first allude to some on the subject to which I was referring in my last paragraph.

Milk.—The vexed question whether pepsin and rennet are different enzymes or not still continues to excite interest. The pros and cons are about equally balanced if one counts numbers; but when one looks to the authoritative quality of the writers, the balance of evidence this year, at any rate, appears to be in favour of the old view that the two enzymes are distinct. The most convincing of these papers is that which has been written by the veteran Olof Hammarsten,[20] who from the first has disputed Pawloff's view that the two enzymes are identical. One is glad to see that Hammarsten, who has resigned his professorship, is still active in research. He has continued, for example, his work on the bile of the rarer animals, and this year has investigated that of the hippopotamus,[21] and found that further varieties of bile acids exist in the animal kingdom than those which were previously known. He has also since his retirement produced a new edition of his well known text-book,[22] and that has been followed by an English translation by Professor Mandel.[23]

To some extent the milky mantle has fallen upon Professor Hammarsten's successor at Upsala, Professor Hedin, who contributes a paper on the "Specific Inhibition of Rennet and Differences between Rennets."[24] He finds that by warming neutral infusions

on the subject will be found in a paper by Bang (*Skand. Archiv. Physiol.*, 1911, **25**, 105; *A.*, i, 826).

[20] *Zeitsch. physiol. Chem.*, 1911, **74**, 142; *A.*, ii, 998.

[21] *Ibid.*, 123; *A.*, ii, 1010.

[22] "Lehrbuch d. physiol. Chem.," 7th edition, Wiesbaden, 1910.

[23] "Textbook of Physiol. Chem.," translation of the above, Wiley, New York, 1911.

[24] *Zeitsch. physiol. Chem.*, 1911, **74**, 242; *A.*, ii, 998.

of the gastric mucous membrane of the guinea pig, calf, and pike with dilute ammonia and then neutralising, substances are formed which inhibit rennetic action, but the inhibitory substances only inhibit the rennet of the animals used. The conclusion is drawn that this specific action indicates that the enzymes they inhibit are specific also. This conclusion would have been strengthened if it had also been shown that the rennet, say, of the calf did not produce curdling of the milk of other animals. There is no word about this; in fact, all the evidence points the other way; so far as is known, the rennet from any animal will curdle any species of milk.

Heat Coagulation of Proteins.—This question has been taken up by Dr. C. J. Martin and Miss Chick.[25] They show in the new light shed by physical chemistry on colloids, and in the new language of that science, that many of the old facts become intelligible. Heat coagulation is not a mere temperature effect, but is really a reaction between protein and water, and is influenced by temperature in accordance with the law of Arrhenius, the temperature-coefficient, however, being a very high one. This "denaturation" of the protein is followed by the separation of the altered protein in particulate form (agglutination). The first step, denaturation, is, if means are taken to prevent changes in acidity, a reaction of the first order; as the protein is precipitated, free acid is progressively removed from the solution, and this second change, "agglutination," occurs more rapidly than the denaturation. A number of other issues are discussed, such as the influence of salts on the phenomenon, but these the reader must discover for himself. My object is fulfilled by calling attention to this interesting research.

The Use of Elastin for Isolating Pepsin.—The annual output by Abderhalden and his colleagues continues unabated. Most of it is useful spade work, working out details on the lines of previous researches: the digger may chance to unearth a precious stone now and then. Abderhalden's[26] precious stone this year is the discovery of the usefulness of elastin for the isolation and detection of pepsin. It has long been known that if fibrin is placed in a solution containing pepsin, the enzyme is adsorbed and removed, and can be subsequently washed out from the fibrin. Elastin and other solid proteins act in a similar way, but the special advantage of elastin is its comparative insolubility in digestive juices, so that subsequently the enzyme can be obtained almost free from proteolytic products. Other enzymes are adsorbed in a similar way, but so far Abderhalden has confined his work almost exclusively to pepsin.

[25] *J. Physiol.*, 1910, **40**, 404; *A.*, 1910, i, 597; *ibid.*, 1911, **43**, 1; *A.*, i, 822.

[26] *Zeitsch. physiol. Chem.*, 1911, **71**, 315, 339, 449; **74**, 67, 411; *A.*, i, 511; ii, 506, 999.

By this method it has been shown that proteolytic enzymes are absent from the fæces, but by far the most important result obtained is the presence of pepsin in an active form in the intestine, into which it is carried and protected by the elastin or other comparatively insoluble proteins of the food. Hitherto, it has generally been supposed that the action of pepsin ceases beyond the confines of the stomach. There is still a large amount of ignorance in relation to the individual parts played by pepsin, trypsin, and erepsin in protein cleavage, but it can hardly be doubted that in clearing away this ignorance investigators will have in the future to consider a new factor, namely, the co-operation of the gastric enzyme pepsin with the others in the much more complete digestive process which takes place in the small intestine.

Origin of the Hydrochloric Acid of the Gastric Juice.—Passing next to the inorganic ally of pepsin, we come across an interesting paper by Miss Fitzgerald.[27] Many workers have employed various microchemical tests in order to localise the seat of formation of the acid of the gastric juice, and although the evidence available clearly points to the association of acid formation with the parietal or oxyntic cells of the gastric tubules, no absolute certainty has been attained; neither has it been proved beyond cavil that hydrochloric acid exists in demonstrable form in the secretion before it reaches the free surface of the mucous membrane. This has now been finally set at rest. Solutions containing potassium ferrocyanide and ammonium ferric citrate were injected into rabbits and guinea pigs, and the animals were killed from three to thirty hours later. This mixture readily formed Prussian blue with hydrochloric acid of a much less concentration than that contained in gastric juice, but gave no reaction with sodium phosphate or carbon dioxide. Microscopic sections of the stomach showed the presence of Prussian-blue in the lumina of the gland tubules and in the canaliculi of the parietal cells. The acid is thus shown to be already in a free state in the secretion of the cells which form it. A faint blue coloration throughout the protoplasm of the same cells seemed to indicate its presence there too. The chemical operations involved in the liberation of the free acid from chlorides is another question altogether; but excess of chlorides in the parietal cells as compared with the amount in the pepsin-forming cells was shown to be present.

The Physiological Protein Minimum.—I do not mean here to re-open the old question which the name Chittenden suggests, but to look at the subject from another point of view. During starvation the loss of nitrogen per day soon reaches a constant level,

[27] *Proc. Roy. Soc.*, 1910, B, 83, 56; *A.*, ii, 50.

and in this condition it might be thought that if protein were administered in such amount that its nitrogen equalled the loss, the drainage of nitrogen from the body would be arrested. The classical experiments of Voit showed, however, that nitrogen equilibrium is not reached until the amount given is two or three times greater than the amount lost during inanition. In 1909 Louis Michaud [28] attacked this problem afresh, using dogs, as Voit did in his experiments, with the conclusion that the result varies according to the sort of protein used in feeding. A mere nitrogen estimation in the food protein is not enough; the value of a protein depends rather on the proportion between its cleavage products. If a protein foreign to the body, such as edestin, is used, equilibrium was not reached until excess was given as stated by Voit. But if the food protein employed was the flesh or other tissues of another dog, then equilibrium is reached more easily; in fact, it can be attained by giving just enough to replace the inanition daily waste. Horse flesh or casein were intermediate between edestin and dog's flesh in this relationship.

This paper attracted much attention, and, put in a sentence, the main conclusion is that a live dog can make its tissues most easily from dead dog. If this were pushed to a logical conclusion, we might even formulate a scientific defence of cannibalism. However likely such a conclusion might appear to the superficial thinker, it would really upset much of the recent knowledge acquired by painstaking work on protein metabolism. We know with almost absolute certainty that a small fraction only of the protein ingested is actually used as a "flesh-forming food"; the larger fraction is almost immediately cast out as waste in the form of urea. It is, however, quite conceivable that this waste might be lessened by using protein food as near as possible in composition to the protein tissues peculiar to the species of animal under observation.

A good many people have taken up the point. Frank and Schittenhelm [29] confirm the general idea; they find that the minimum amount of protein capable of maintaining nitrogenous equilibrium after inanition is appreciably less when the protein administered is the protein of dog's muscle than it is when any other kind of protein is employed for feeding purposes. Other workers,[30] however, find that the advantage of feeding dog on dog, although present, is not a very great one. This is what one would rather have anticipated. Even Frank and Schittenhelm [31] found in their further

[28] *Zeitsch. physiol. Chem.*, 1909, **59**, 405; *A.*, 1909, ii, 498.

[29] *Ibid.*, 1910, **70**, 98; *A.*, ii, 127.

[30] See, for instance, von Hoesslin and Lesser, *ibid.*, 1911, **73**, 345; *A.*, ii, 904. Also London and Rabinowitsch, *ibid.*, 1911, **74**, 312; *A.*, ii, 999.

[31] *Ibid.*, 157; *A.*, ii, 904.

work that in ordinary nutrition (apart from inanition) nitrogenous metabolism runs practically the same course, whatever form of protein was given in the food.

Synthesis of Amino-acids in the Body.—A series of papers initiated by Franz Knoop on this subject bids fair to yield important results. He showed [32] that α-amino-acids after parting with their amino- and carboxyl groups are broken down in a manner similar to the next lower fatty acid, and that they may be acetylated in the bodies of animals. Further, α-ketonic acids may take up nitrogen in the body with the production of optically active α-amino-acids; α-hydroxy-acids may also be converted into α-amino-acids. Embden and Schmitz,[33] by means of perfusion experiments on the liver, discovered that *p*-hydroxyphenylpyruvic acid was converted into tyrosine by that organ, and that after perfusion with *p*-phenylpyruvic acid, phenylalanine could be isolated in the form of a carbamic acid; leucic acid gave rise to leucine-carbamic acid. If the liver was rich in glycogen, during simple perfusion part of the glycogen gave rise to alanine, lactic acid and pyruvic acid being apparently intermediate products. Knoop and Kertess [34] fed a dog on α-amino-γ-phenylbutyric acid, and its urine contained the *l*-modification of this acid, its acetyl derivative, and *d*-α-hydroxy-γ-phenylbutyric acid. In addition, butyric acid was formed, indicating degradation of the amino-acid through the ketonic acid to the next lower fatty acid. When fed with the α-ketonic acid, the products were *d*-α-hydroxy-γ-phenylbutyric, acetylaminophenylbutyric, and hippuric acids. The formation of the same hydroxy-acid in both instances, and in larger quantity from the ketonic acid, is confirmatory of the view that the amino- is converted into the ketonic acid in the animal body. The acetylamino-acid is also in each instance derived from a probably inactive intermediate compound, and not by direct acetylation, as Neubauer and Warburg [35] considered to occur in perfusion experiments on the dog's liver.

The Corpus Luteum.—The year's work contains a good deal about internal secretions in general, and adrenaline in particular, but I pass from these to consider one point only. It is well known that after the exit of the ovum from the ovary, its follicle is filled up by the growth of yellow-coloured cells, and that the corpus luteum so formed attains a great size if pregnancy ensues. It has been generally assumed that these cells form a "hormone," and the function generally attributed to this chemical messenger is to assist

[32] *Zeitsch. physiol. Chem.*, 1910, **67**, 489; *A.*, 1910, ii, 880.
[33] *Biochem. Zeitsch.*, 1910, **29**, 423; *A.*, ii, 53.
[34] *Zeitsch. physiol. Chem.*, 1911, **71**, 252; *A.*, ii, 514.
[35] *Ibid.*, 1910, **70**, 1; *A.*, ii, 53.

in some way in the successful fixation of the ovum in the uterus. Another series of observations on the causation of growth in the mammary glands, culminating in milk production, failed to reveal the presence of any secretory nerves in the milk glands, corresponding with what are known to exist in the salivary and sweat glands; and evidence that mammary growth occurs in cases where there can be no possible nervous connexion between the generative organs and the mammary glands pointed to the conclusion that the correlation must here be chemical rather than nervous. A few years ago Professor E. H. Starling, working with Miss Lane-Claypon, thought that the hormone in question must be secreted by the fœtus, because injection of fœtal extracts led to a somewhat imperfect hypertrophy of mammary tissue. Doubt was, however, felt in many quarters whether this could be the whole explanation, for mammary evolution occurs in many virgin animals, in which ovulation is not followed by pregnancy. C. H. O'Donoghue[36] has investigated the question recently in the Marsupial cat known as Dasyurus, which from many points of view, into which it is unnecessary to enter here, is a particularly suitable animal for the solution of the problem. He finds a close correspondence between the stages in the development of the corpus luteum and the mammary glands, and finally concludes that it is the hormone secreted by the former which is the inciting cause of the growth of the latter.

On the other hand, F. H. A. Marshall,[37] who has investigated a similar question in the dog, arrives at the conclusion that the internal secretion from the ovary, which brings about "heat," originates in the interstitial cells of that organ. It is quite possible that the ovary may form more than one internal secretion, and only one of these acts on the mammary glands.

The Effect of Choline on Blood Pressure.—Mott and I appear to have been the first to recognise the physiological and pathological importance of choline. It is a base derived from the cleavage of certain phosphatides, notably lecithin. Its presence in such fluids as that which bathes the spinal cord and brain would be a tangible proof of the disintegration of nervous matter such as occurs in many of the grosser diseases of these organs, for phosphatides here are much more abundant than in other tissues. Many physiologists have taken up the choline question, and some have entirely denied the existence of choline in the cerebro-spinal fluid, even after

[36] *Proc. physiol. Soc.*, 1911, xvi.; *J. Physiol.*, **43**; *Quart. J. Micro. Science*, 1911, **57**, 187. Another paper on the corpus luteum calls attention to certain toxic effects produced by a lipoid substance that can be extracted from it (Bouin and Ancel, *Compt. rend.*, 1910, **151**, 1391; *A.*, ii, 129).

[37] *Proc. physiol. Soc.*, 1911, xxi; *J. Physiol.*, **43**.

massive disintegration. It may be freely admitted that the tests hitherto devised for identifying the base are only relatively conclusive, for sufficient material has never been collected for a complete analysis. All, however, seem now to admit that the material which is undoubtedly present and so distinguishes the pathological from the normal fluid, is, if not choline itself, a substance nearly related to it, perhaps a derivative of choline, and the latest theory advanced is that it is trimethylamine, a cleavage product of choline.[38] This is a question quite apart from that of cholesterol, which all admit is present in cerebro-spinal fluid in cases of chemical breakdown of nervous tissues.

Another point in relation to choline is whether, when injected into the blood stream, it produces a rise or a fall of blood-pressure. This ought not to be a difficult question to answer. The operative procedure is simple, and the preparation of pure choline or of its hydrochloride presents no great difficulties. The majority of observers are agreed that the effect is a fall of arterial pressure in accordance with the original statements of Mott and myself.[39] But the question has curiously enough raised a keen and bitter controversy, because certain observers in Russia, Modrakowski and Popielski,[40] have persistently maintained that everybody except themselves is wrong, and that the typical effect of an injection of choline is to raise arterial pressure, and that the opposite result obtained by others is due to their having used impure materials. One always distrusts observers who claim for themselves a monopoly in the capacity to carry out correctly a simple piece of chemical analysis or physiological experimentation, and one cannot therefore be sorry for the wholesome castigation administered to Popielski and his colleagues by Abderhalden and F. Müller.[41] This is not by any means the first of their papers dealing with the subject, but it is the most thorough, and will in the minds of all reasonable people settle the question once and for all. Some of their preparation was sent to Popielski in order that he might test the matter for himself, and he reported that it produced a rise of blood-pressure. Unfortunately for Popielski, the specimen sent (by mistake) was an impure one, which according to him should have produced a fall of blood-pressure. It did produce a fall of pressure in Berlin, and so did the pure specimen. Many strange things have

[38] C. Dorée and F. Golla, *Bio-Chem. J.*, 1911, **5**, 306; *A.*, ii, 212.

[39] These observers have recently been joined by the following: E. Berlin (*Zentr. Physiol.*, 1910, **24**, 587; *A.*, ii, 516) and A. Lohmann (*Zeitsch. Biol.*, 1911, **56**. 1; *A.*, ii, 630).

[40] Popielski's most recent paper will be found in *Zeitsch. physiol. Chem.*, 1910, **70**, 250; A., ii, 124.

[41] *Ibid.*, 1911, **74**, 253; *A.*, ii, 994.

occurred on the Russian frontier, but this transformation surely beats the record.

Manganese and Vanadium as Constituents of Animal Tissues.—Everyone acquainted with the history of chemistry will remember that the element phosphorus was first discovered in an animal product, namely, urine. It was not until nearly half a century later that it was found in the mineral kingdom. This discovery in the eighteenth century evoked as much interest in the scientific world as the discovery of radium has done in our own day. As a rule, however, the discovery of new elements occurs in the inorganic world, and later on search is made for them in animal tissues, and the list of the elements present in the latter thus grows in length. The discovery of iodine, however, in 1811 dates from the investigation of sea-weeds, and it was not until about twenty years ago that Baumann showed that it is also present in organic combination in the secretion of the thyroid gland in animals. The long list of elements found in animal tissues must now have added to it two more, namely, manganese and vanadium. The presence of manganese in such tissues which had been occasionally noted in the past was attributed to accident; and manganese, like copper and lead, was therefore supposed to be due to contamination with the material used in utensils employed for cooking, etc., or to the use of drugs. No doubt in the majority of instances this is the correct explanation. Copper, however, we now know is contained in at least two physiological proximate principles, namely, hæmocyanin, the blue pigment in the blood of many crustaceans and molluscs, and turacin, the red pigment in the feathers of the plantain-eating birds.

It now seems equally necessary to include manganese as a normal body constituent in certain forms of animal life. According to Piccinini,[42] it occurs in varying quantities in the different tissues of the animal and human organism. It is obtained from the food, but does not disappear when a diet free from it is taken. The addition of manganese to the diet is also stated to increase the iron of the blood, liver, and spleen. One would hesitate from this description to include manganese among the normal constituents of the body; its presence partakes more of the accidental order. and like many poisons, although manganese itself produces no obvious toxic symptoms in these doses, it appears to remain in the tissues, and is excreted with difficulty. But in the case of certain aquatic animals there is a different story to relate. Its presence in the fresh-water mussels or clams, Unio and Anodon, was first noted by Bradley in 1907,[43] and in their eggs. His promise to

[42] *Arch. farm. sperim.*, 1910, **9** ; *A.*, ii, 622.
[43] *J. Biol. Chem.*, 1907, **3**, 151 ; *A.*, 1907 ii, 567.

investigate the source of the metal and its physiological meaning was only fulfilled last year.[44] He found that the element can be detected in most of the organs of the mussel, but is most abundant in gills and mantle. The source of the element is the food these animals ingest; and that, of course, is the source of any other substance found in the body. They feed on crenothrix and diatoms, which are able to concentrate manganese from its very dilute solution in the water. In lakes where the water is very pure neither crenothrix nor mussels are found, nor do they live if placed there; the manganese has probably a respiratory function in the tissues and blood of these lamellibranchs, much as iron has in our own blood.

No one had previously dreamt that the comparatively rare metal vanadium was a possible constituent of animal structures, but Henze[45] has found it in the blood-corpuscles of certain ascidians, Phallusia being the animal he made most of his observations on. These corpuscles are extremely acid to litmus, and the acid is in large part volatile with steam, and probably organic. On exposure to air, the corpuscles turn yellowish-green to blue; the chromogen of this pigment is soluble in water and in acetone; in time it turns brown. On incineration it yields about 15 per cent. of vanadic acid (V_2O_5). This is just one of those discoveries which impresses the imagination; even in the well-tilled field of bio-chemistry there are doubtless plenty of discoveries still awaiting discoverers.

Physiological Climatology.—This paper by Professor Osborne, of Melbourne,[46] is the first of what promises to be an instructive and interesting series. It illustrates the usefulness of long holidays and opportunities for travel. One compensation we have in the migration of some of our younger physiologists to the colonies is that in new atmospheres they see things in fresh lights. The particular subject treated of in the paper under consideration is the relation of the loss of water from the skin and lungs to the external temperature in actual climatic conditions. The usual text-book statement that heat lost by radiation and conduction from the skin makes up the greater portion of the heat lost from the body, is only true under certain conditions; an air-temperature equal to that of the body would reduce this loss to zero. If the metabolism of the body is constant during rest, and the heat production therefore is fairly constant too, it follows that if the air-temperature is raised, and loss by radiation and conduction consequently lessened, the heat loss due to evaporation must make up the balance; other-

[44] *J. Biol. Chem.*, 1910, **7**, xxxvi, and **8**, 237; *A.*, 1910, ii, 731, 979.
[45] *Zeitsch. physiol. Chem.*, 1911, **72**, 494; *A.*, ii, 740.
[46] *J. Physiol.*, 1910, **41**, 345; *A.*, ii, 124.

wise heat accumulation will occur, and the body temperature will rise. It would be expected, therefore, that the water loss would be a linear function of the air temperature. This simple relationship, however, does not occur, and the cause of the perturbations in the straight line is not clothing, but is more complex; one factor, at any rate, is the humidity of the air, and another is the velocity of its movement. If the air is dry and in movement, it will tend to dry the skin, and if body temperature and skin inbibition are to be kept constant, then the metabolism must be augmented. What apparently does occur is a compromise: the skin loses some of its water of imbibition, and the metabolism undergoes a moderate rise. This explains the unpopularity of the east wind in N.W. Europe.

Another factor is the amount of ventilation *via* the lungs; this is increased when the atmospheric temperature is high, and is known familiarly in the lower animals, as when a dog pants in the summer time. How the respiratory centre is affected by a high air-temperature is a puzzle, for the body temperature does not rise; possibly the carotid blood may become heated in its passage up the neck.

Osborne also found that the carbon dioxide excreted varies directly, not inversely, as the external temperature. The increase in pulmonary ventilation will in part explain this; more carbon dioxide is produced from the additional work of the respiratory muscles, and more is "washed out" from the tissues. There is, further, some indication that the respiratory quotient rises with rising shade temperature. Harvey Sutton found this quotient approached unity when the wet-bulb thermometer rose in a room he could artificially make warm and moist, and made some suggestions regarding the relation of this reaction to the preponderance of carbohydrates in the diets of tropical aboriginals.

This imperfect and hasty outline of the paper will at least indicate its practical importance, and make us await with interest further contributions on the subject from its author.

Creatine and Creatinine.—I had intended at this point to insert a brief review of the somewhat voluminous work on this subject which has appeared throughout the year. Looking through the papers once more, however, I find little or nothing that throws new light on the very puzzling metabolic problem that these substances present. New facts have been elicited, for instance, the indispensability of carbohydrate food for maintaining the normal course of creatine-creatinine metabolism, a function which is not exercised, either by fats or by proteins.[47] Such facts, however, and

[47] L. B. Mendel and W. C. Rose, *J. Biol. Chem.*, 1911, **10**, 213; *A.*, ii, 1002.

others (often conflicting) too numerous to mention are difficult to bring into line with each other, or with any general view of the real history of these substances in the body. For this reason, as well as exigencies of space, I prefer to leave the subject to some future time when the difficulties that surround the subject are more fully cleared up.

The Lipoids.—For much the same reasons, I think it would be better to omit more than a passing reference to the lipoids. They continue to exercise a great attraction for the researcher, although there is some indication that the actual number of papers about them shows a diminution this year. The work done has been useful and painstaking, but in the main is directed to the working out of details; so here again the subject hardly lends itself to general discussion. As examples of the nature of the work in progress, we may take that of Professor Lorrain Smith[48] on the staining reactions globules of fat and lipoid undergo in microscopic technique; on methods of estimating such substances by the same author;[49] a separation of the lipoids of egg-yolk,[50] and so forth. It is not many years back that I devoted a considerable space of one of my reports to the lipoids, and the subject is obviously one that can wait further and fuller development in the future.

This leaves me free now to take up the last section of my report, as outlined in its opening, and take up seriatim the three subjects chosen there for more extended treatment.

Nucleic Acid and Nucleases.

In this instance I make no apology for returning to a subject I have treated at length in former reports. For here a considerable advance has recently been made, and our knowledge, both of the chemical composition of nucleic acid and of its fate in the body, is increasing by leaps and bounds.

At the risk of wearying some readers who have studied my previous reports, I will briefly recapitulate what was known at this time last year, in order to give some degree of completeness to my story.

Nuclein is the name originally given by Miescher in 1871 to the main constituent of the nuclei of cells. He recognised that it was a nitrogenous phosphorised organic substance in union with a protein. The non-protein constituent of the complex has since been known as nucleic acid. Making rather a long jump to a later epoch, Kossel isolated and identified many of the cleavage products

[48] *J. Path. Bact.*, 1910, **15**, 53; *A.*, ii, 57.

[49] *Ibid.*, 1911, **16**, 131; *A.*, ii, 1006.

[50] Serono and Palozzi, *Arch. farm. sperim.*, 1911, **11**, 553; *A.*, ii, 1005.

of nucleic acid, and he separated out phosphoric acid and certain crystalline bases, and noted in addition the presence of a carbohydrate. The bases Kossel mainly worked at are those which were named purine bases by Emil Fischer, and the four principal ones are hypoxanthine (mono-oxypurine), xanthine (dioxypurine), adenine (aminopurine), and guanine (amino-oxypurine). At first it was supposed that there were four nucleic acids, each of which yielded a different base.

Later other bases were separated out, which are derivatives of another cyclic nucleus, namely, pyrimidine.

The work of Walter Jones, Levene, Steudel, and others showed that ordinary nucleic acid yields two bases of the purine group, namely, adenine and guanine, and two of the pyrimidine group, namely, thymine (diketomethylpyrimidine) and cytosine (aminopyrimidone). Other bases when present are due to secondary reactions. The identity of the carbohydrate was a matter of dispute, some regarding it as a pentose, others as a hexose. Kossel regarded it as a hexose mainly because he obtained from nuclein a yield of lævulic acid.

Steudel appears to have been the first to present a provisional but complete view of the structure of the constitution of the nucleic acid molecule. He thought it consisted of a chain of four atoms of phosphorus, each of which was united on the one side to hydroxyl, and on the other to a hexose molecule. Each of the four hexose groups in its turn was united to a base, a different base for each hexose group.

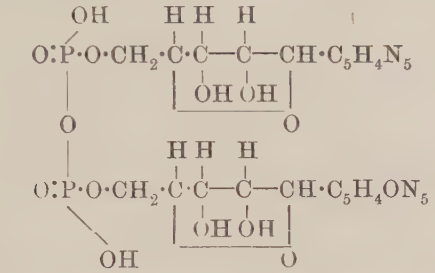
Almost simultaneously with this work, that of Bang showed the existence in certain organs of a simpler form of nucleic acid, which yielded on decomposition only three substances, namely, phosphoric acid, a sugar of the pentose group, and one purine base, guanine. This was consequently termed guanylic acid.

This brings us to the work of the years 1910 and 1911, and the more chemical aspect of the subject is discussed in a series of papers published in the *Berichte* by Levene and his colleagues.[51] One important point they made out was the identity of the carbohydrate; it is ribose, one of the pentoses. Levene and Jacobs[52] very successfully defend this view against certain criticisms of Neuberg on this question. Without going fully into the complicated problem of how the linking together occurs, one may give the main view taken by these workers, and the new nomenclature they have introduced.

A nucleic acid is designated a *nucleotide*; thus Bang's guanylic

[51] *Ber.*, 1910, **43**, 3150, 3164; 1911, **44**, 746, 1027; *A.*, ii, 96, 408, 510.
[52] *Ibid.*, 1910, **43**, 3147.

acid, which yields on hydrolysis only one molecule of ribose and one base (guanine), is a mono-nucleotide. As the number becomes 2, 3, or more, we get di-, tri-, etc., nucleotides; thus the part of the molecule which yields the two purine bases, adenine ($C_5H_5N_5$) and guanine ($C_5H_5ON_5$), may be represented by the following formula:



By splitting off the phosphoric acid, what is left are the two combinations of ribose and base; that is, ribose + adenine and ribose + guanine. Such compounds are termed *nucleosides*; it is unfortunate that nucleotide and nucleoside are names that are so much alike, for it will be difficult to remember which is which. These two nucleosides are named guanosine and adenosine respectively. By hydrolysis with acids the bond between the sugar and the base is dissolved, guanosine yielding guanine and α-ribose, and adenosine adenine and *d*-ribose. These two nucleosides may also be spoken of as *aminonucleosides*, because the base in each case contains the amino-group. By the action of nitrous acid the two amino-nucleosides are converted into the corresponding hydroxy-nucleosides by removal of the amino-group; thus guanosine yields xanthosine (xanthine + ribose) and adenosine yields hypoxanthosine (hypoxanthine + ribose), also spoken of as inosine, another confusing item in the new nomenclature. It will be noted I have not complicated the account of this work by introducing the pyrimidine compounds of ribose, such as cytidine, that is, cytosine + ribose, about which less is known, but in which the linking is apparently not glycosidic.

Passing now to the physiological or metabolic side of the question, we have to inquire whether within the body disintegrations occur which are similar to those which we have just seen can be produced by chemical reagents. The answer is "Yes," and the agents at work in the body are enzymes, to which one may give the general name *nucleases*.

Before describing the details of this aspect of the subject, let us return for a moment to history; but it is only necessary for my purpose to go back to 1909, in which in my report I stated

the following to be an outline of what was then known.[53] I reproduce the paragraph almost verbatim.

"The decomposition is accomplished by certain tissue enzymes which have been studied in extracts of tissues and organs. Their distribution varies a good deal, both in different animals and in their different organs, but, speaking generally, they are most abundant in the liver, spleen and kidney.[54] The first to act is called *nuclease*; it liberates the purine bases from nucleic acid. The next to come into play are called deamidising enzymes, because they remove the amino-group; one of them, *adenase*, converts adenine into hypoxanthine (mono-oxypurine); the other, called *guanase*, converts guanine into xanthine (dioxypurine); finally, *oxydases* step in, which transform hypoxanthine into xanthine, and xanthine into uric acid (trioxypurine). But even this does not bring the long list to a conclusion, for in certain organs (for example, the liver) in many animals there is a capacity to destroy the uric acid after it is formed, and the enzyme responsible for uric acid destruction, and which normally protects the animal from a too great accumulation of this substance, is called the *uricolytic enzyme*."

Now this was complicated enough in all conscience, but further investigation in the light of the new knowledge we now possess of the chemistry of nucleic acid has shown that in reality it is more complex still.

Starting at the beginning, that is, when nucleic acid enters the body with the food, our first question is how far its disintegration proceeds in the alimentary canal. Previous work on this question has mainly consisted of investigations *in vitro*. We are able now to record experiments carried out by the more satisfactory method of experiments on the living animal. This was done by E. S. London and Schittenhelm,[55] who employed dogs with appropriate fistulæ for the purpose. They found that nucleic acid is neither altered nor absorbed in the stomach, but that it is to some extent split up in the intestine; a small amount of purine bases is liberated, but the major amount of the nucleic acid given is only broken down as far as the mono-nucleotide or nucleoside stage, and these are absorbed lower down the intestinal tube. In a later research,[56] they succeeded in isolating guanosine, and identifying it with certainty; they, however, agree with Levene and Jacobs, to whose

[53] *Ann. Report*, 1910, 170.

[54] Fresh facts under this heading are contained in a paper by Juschtschenko, *Biochem. Zeitsch.*, 1911, **31**, 377; *A.*, ii, 412.

[55] *Zeitsch. physiol. Chem.*, 1910, **70**, 10; *A.*, ii, 52.

[56] *Ibid.*, 1911, **72**, 459; *A.*, ii, 745.

work we shall pass immediately, that the final splitting occurs in the organs and tissues.

Levene and Medigreceanu [57] made their experiments *in vitro* with the natural juices supplied to them by Pawloff. They found also that nucleotides were changed into nucleosides by intestinal juice, but that pyrimidine nucleotides were less affected than guanylic acid (guanine nucleotide); the nucleosides (inosine, guanosine, cytidine) were not affected by any digestive juice.

We may therefore conclude that during digestion the total amount of cleavage is small.

This brings us to actual metabolic experiments and the investigation of the action of tissue extracts. Here I have six important papers to discuss, all emanating from America, some from Levene's and some from Walter Jones's laboratory. I will take them in chronological order.

The first on the list, "Nuclein Metabolism in the Dog," is by Levene and Medigreceanu.[58] It deals with the effect seen in the urine as a result of feeding on nuclein and some of its cleavage products. When nucleic acid is given, 50 per cent. appears in the urine, of which 85 per cent. is in the form of allantoin, and the rest as urea. If thymus gland is given, 17 per cent. of the nitrogen is excreted as allantoin, 5 per cent. as uric acid, and the rest urea. Various purine bases were given, and certain nucleosides, such as inosine; varying fractions of the nitrogen in urea, allantoin, uric acid, etc., were obtained. These results clearly show that in spite of the small change produced in the alimentary canal, the nuclein group of substances are nevertheless broken down into simpler materials somewhere in the body; it is obvious that this somewhere must be in the tissues and organs.

The same authors [59] then proceeded to investigate the various tissue juices, or plasmata, as they term them. It is only necessary to give a few samples of their results. Plasma of heart-muscle, liver, kidney, and intestinal mucosa hydrolyse inosine or hypoxanthosine, giving rise to the free base and *d*-ribose; blood-serum and pancreas-plasma have no effect. Guanylic acid is hydrolysed by the same plasmata, with the addition of that obtained from the pancreas. Cytidine (cytosine + ribose) was not split by any plasma investigated, and the cleavage of nucleic acid from yeast was incomplete. Such work at once demonstrates that various tissues may act in different ways, and indicates that the enzymes are numerous and differently distributed in the organs.

[57] *J. Biol. Chem.*, 1911, **9**, 375; *A.*, ii, 744.
[58] *Amer. J. Physiol.*, 1911, **27**, 438; *A.*, ii, 303.
[59] *J. Biol. Chem.*, 1911, **9**, 65; *A.*, i, 410.

This view was accentuated in the third paper I have to refer to, this time from the pen of Walter Jones.[60] He regards the use of the term nuclease as unsatisfactory if it is understood to mean an enzyme which liberates purine bases from nucleic acid, for there is no assurance that the enzyme of one gland can decompose the nucleic acid of another organ. Although the nucleotide structure is common to all the nucleic acids, differences occur in the nature and number of their nitrogenous rings, and it would therefore be surprising if one enzyme can decompose them all, for the more one learns about enzymes the greater appears to be their specificity. Illustrating this, he found that an extract of ox spleen will effect the decomposition of the mono-nucleotide guanylic acid, but that pig's pancreas which is rich in other kinds of nuclease has no effect on this particular nucleic acid.

As a further illustration of the multiplicity of the enzymic agents at work, Jones in his next paper[61] considers the case of the deamidases, and shows that there are at least four independent ones. We must add to the adenase and guanase, which were known before, two others, namely, guanosine-deamidase and adenosine-deamidase. Their actions are indicated by their names; thus adenase converts adenine into hypoxanthine; adenosine-deamidase converts adenosine into hypoxanthosine; guanase converts guanine into xanthine; guanosine-deamidase converts guanosine into xanthosine. The enzymes acting on the amino-purines are distinct from those which act on the amino-nucleosides, because one group is present in pig's liver, for instance, and the other is not.

The next contribution to the subject takes us back again to Levene and Medigreceanu.[62] They accept the work of Jones, and of similar results obtained in Germany by Schittenhelm, and which coincides with their own results in regarding the gradual series of changes that occur in nucleic acid, as being due to the graded action of numerous and specific enzymes, and they classify the nucleases into three groups as follows:

(1) *Nucleinases*, which resolve the molecule into mono-nucleotides; these occur in all organs, in pancreatic juice, but not in gastric juice.

(2) *Nucleotidases*, which liberate phosphoric acid, leaving the ribose-base complexes (nucleosides) intact. These also occur in all organs, and in intestinal juice, but are absent in gastric and pancreatic juices.

(3) *Nucleosidases*, which hydrolytically cleave the nucleosides

[60] *J. Biol. Chem.* 1911, **9**, 129; *A.*, i, 410.
[61] *Ibid.*, 169; *A.*, i, 410.
[62] *Ibid.*, 1911, **9**, 389; *A.*, i, 698.

into their components, ribose, and bases of the purine or pyrimidine groups. These are absent in all the digestive juices, and in the plasma or tissue juice expressed from the pancreas, but are present in varying degree in the plasmata of most other organs.

I now reach the last paper on the question, and this is a very comprehensive one by W. Jones and S. Amberg.[63] These writers again emphasise the points already noted relating to the multiplicity and specificity of the enzymes at work. To show the differences between different organ extracts, let us take the following as an instance. The pancreas and the liver of the pig were both employed to act upon nucleic acid. In the pancreas experiment, guanosine was one of the end-products, but this nucleoside underwent no further cleavage; adenosine was formed simultaneously, but this was deamidised to form hypoxanthosine or inosine. In the experiment with pig's liver, guanosine was not only deamidised to form xanthosine, but the xanthosine was further split into ribose and xanthine. At least nine enzymes are in this way called into play:

(1) Phospho-nuclease.
(2) Purine nuclease.
(3) Guanosine deamidase.
(4) Adenosine deamidase.
(5) Adenase.
(6) Guanase.
(7) Xanthosine hydrolase.
(8) Inosine hydrolase.
(9) Xantho-oxydase.

We further see that this clears up another difficulty I alluded to in a previous report,[64] namely, how does hypoxanthine occur in muscle, seeing that adenase is absent from that tissue? The provisional answer given at that date was that hypoxanthine in this situation is "preformed," and is not directly connected with nuclein metabolism at all. We have now another possibility, and a much more probable one, and that is that adenosine is deamidised to hypoxanthosine (or inosine) by the enzyme numbered (4) on the foregoing list; and this is hydrolytically split so as to yield hypoxanthine by enzyme No. (8) on the list. Enzyme No. (5) in this case never comes in at all.

Finally, let me attempt briefly to summarise:

(1) Nucleic acids possess a common structure, namely, phosphoric acid combined with a carbohydrate (the pentose named ribose), which in its turn is united with a base.

[63] *Zeitsch. physiol. Chem.*, 1911, **73**, 407; *A.*, ii, 823.
[64] *Ann. Report*, 1910, 171.

(2) They differ from each other by such grouping being either single or re-duplicated.

(3) The general term nucleotide is adopted for the phosphoric acid–ribose–base complex.

(4) Nucleic acids may be mono-nucleotides; for instance, guanylic acid; but more usually the grouping is re-duplicated to form poly-nucleotides.

(5) The bases obtainable from poly-nucleotides are adenine and guanine of the purine group, and bases of the pyrimidine group, such as cytosine.

(6) In the case of the pyrimidine bases, their union with ribose is possibly not glycosidic, and is firmer than in the case of the purine bases.

(7) When broken down by chemical reagents, the first change is the removal of the phosphoric acid, leaving intact the combinations of ribose and base.

(8) The ribose-base complexes are termed nucleosides; thus:

guanosine = guanine + ribose.
adenosine = adenine + ribose.
cytidine = cytosine + ribose.

(9) The nucleosides may be split hydrolytically into base and carbohydrate; or they may be deamidised, and the corresponding hydroxynucleosides obtained; and these in their turn may by hydrolysis be broken up into base and carbohydrate; for instance, adenosine may be deamidised to hypoxanthosine (also called inosine), and this in its turn is split into hypoxanthine and ribose.

(10) The same cleavages are accomplished in the body by the action of tissue-enzymes contained in varying degrees and kinds in the different organs and tissues. As these enzymes are specific, the number which may come into successive play in the decomposition which occurs within the body is extremely numerous. These enzymes may be spoken of in a general way as nucleases. The individual names they have received indicate the particular act of cleavage they perform.

(11) The nucleic acids in the food are not affected by gastric juice, and in the intestine such cleavage as does occur is limited to their separation into mono-nucleotides, and the partial conversion of these into nucleosides by the splitting off of phosphoric acid.

"Standard Bread."

"Some gave them white bread, and some gave them brown," indicates the existence of a dilemma which caused trouble in past ages, and still continues to be a burning question. The advocates of

bread made from the whole grain, or at any rate from flour which retains the germ, have received support from a section of the daily press during the year; and the irresponsible writers who have considered it their duty to boom what they have illogically termed "standard bread" are more remarkable for their zeal than for their knowledge. The very word "germ" is one to conjure with; to many minds it suggests the germ of life, a sort of concentrated essence of all that is good. To those, however, who desire a sober statement of facts rather than a hysterical presentment of crude ideas, I would recommend an article on the subject by an anonymous writer in a recent issue of *Science Progress*.[65]

There is no doubt that the boom has been beneficial to certain millers, who have been able to sell at high prices inferior flours which would otherwise have been wasted.

There is also no doubt that to the majority of people the choice of white bread or whole-meal bread is altogether immaterial; it is purely a matter of taste to those who live on an ordinary mixed diet, and to whom bread is only one of the many articles of food ingested.

Experiments on rats such as those published in preliminary communications to the weekly medical journals are wholly inconclusive; still less convincing are the hastily compiled statistics by schoolmasters bitten with the craze.

The only logical attitude taken up by a responsible person is that assumed by Dr. F. Gowland Hopkins, and that is that a decision is impossible in the present state of knowledge, and even then the decision will only affect those people to whom bread really is the staff of life. The homeopathists of the past, as is well known, used to prescribe drugs in such extremely minute doses that any physiological action would have been next door to impossible. We, however, are now acquainted with substances such as adrenaline produced in the body which produce powerful effects in doses much smaller than those of the homeopathists. Such materials must ultimately be formed from the food, so that very minute quantities of certain food materials may be important factors in the maintenance of health. The germ of the wheat grain is the part which will ultimately grow when sown into the new plant, and it is quite possible, as Dr. Hopkins has pointed out, that there may be certain substances elaborated by the living cells of the plant which cannot be readily synthesised by the animal body. Their quantity cannot be considerable, and if they are present, and their chemical nature is entirely problematical, it may be that they are nevertheless of value. This is a perfectly feasible hypothesis,

[65] "The Ethics of Food. III. Bread." *Science Progress*, 1911, 536.

and one hopes that some really conclusive experimental work may be set in hand to test its truth. Those who say that whole-meal bread is richer in protein than white bread are speaking the truth, although the difference is not a large one. They forget, however, that chemical composition is never a criterion in itself of the nutritive value of a food. The nutritive value depends on the amount which is assimilated, and that again depends on digestibility, and that can only be determined by actual experiments. To most people whole-meal bread is not so readily digested as white bread is, so that any increase in protein percentage is more than counterbalanced by increased loss in the fæces. Even supposing all the protein in whole-meal bread was entirely digested and assimilated, no one can pretend that the small extra dose of nitrogenous intake can be of the superlative value attributed to it by some; the same end might equally well be obtained by an extra half slice per diem of white bread. The difference is not a quantitative one, but, if present, is qualitative, and the important substance in the germ, if there is one, is in all probability not protein in nature.

A piece of work which illustrates the importance of small amounts of certain food materials in nutrition with another form of food, namely, milk, may be referred to here as a case in point. W. Stepp [66] fed mice on milk deprived of its lipoids; they soon died, but the addition of the alcohol-ether extract to such milk prevented a fatal result. Addition of the fats alone, or of lecithin or cholesterol to such milk did not delay the onset of death. Here, at any rate, we have some unknown substance present in quite small quantity, which is nevertheless essential for successful growth and life.

I have deliberately avoided as much as possible the employment of the popular expression "standard bread," for that term begs the whole question, and assumes beforehand that bread of a certain colour and made in a certain way is to be regarded as an ideal food.

The use of adulterants in all foods should be prohibited by legislation, and offenders should be severely dealt with who attempt to purvey on a credulous public any food to which something has been added or from which something has been removed. It appears hopeless, however, in the present state of politics to attempt any law-making on subjects which affect the public health. Commissions are appointed, and their reports are pigeon-holed for years. The report of the Committee which dealt with food-preservatives ten or twelve years ago is still a dead-letter so far as enactments

[66] "The Importance of Lipoids in Nutrition," *Zeitsch. Biol.*, 1911, **57**, 135; *A.* ii, 1002.

are concerned. The President of the Local Government Board session after session fails to bring to fruition his Pure Milk Bill. These questions unfortunately do not excite Party feeling, and so fall into the background, and *Dreadnoughts* still continue to be built without any steps being taken for ensuring the health of the coming generation who are to man them.

That a standard in white bread is quite as necessary as one in brown bread has been recently brought before the public by the report published by Drs. Hamill and Monier-Williams.[67] In relation to the grosser forms of adulteration which they reveal there can be no difference of opinion that these should be sternly prohibited. Whether bleaching by nitrous fumes is harmful to any serious degree is a moot point. There is some retardation of digestion, especially towards saliva and gastric juice, but the amount of nitrite left in the flour is extremely minute, and in the bread made from the flour it is still further reduced.

Another anonymous article on this subject in *Science Progress*[68] has appeared, and its author rather scorns the evils described, especially bleaching, and takes Drs. Hamill and Monier-Williams to task for condemning such procedure. This I regard as a very unsafe attitude to assume. Our knowledge of the effects of bleaching is still in its infancy; the object of the miller is to supply the public with what they ask for, namely, very white flour, and the consumer runs the risk of the flour being over-bleached, and therefore admittedly harmful, or of obtaining inferior flour made to look like the best, so that the miller reaps a pecuniary reward to which he is not entitled.

The stringent laws of the United States against the employment of adulterants of this order meet with my entire sympathy, for if they err at all it is an error on the right side, as they prevent the introduction of even the thin end of the wedge.

The following brief extract from a judgment by Mr. Justice Warrington in a case tried before him two years ago may be of interest. The case in question was one between rival patentees in the matter of flour-bleaching.

"Even Dr. Halliburton did not go further as a summary of what he considered to be the result, than that the process of treatment by the plaintiff's invention imposes on the human frame just one more of those extra burdens which the progress of civilisation has from time to time imposed on the human frame. Many

[67] "Reports to the Local Government Board on the Bleaching of Flour and the addition of so-called Improvers to Flour." By J. M. Hamill and G. W. Monier-Williams. *Food Reports*, No. 12 (Cd. 5613), No. 14 (Cd. 5831). See also in a more condensed form, *J. Hygiene*, 1911, **11**, 142, 167; *A.*, ii, 1001. [68] 1911, 279.

of us think that there are many modern improvements, the introduction of motor-cars, for example, which impose an extra strain on the human frame, but no one would pretend to say that a patent for the invention of a motor-car would not have been a useful invention for that reason. With regard to digestibility, it seems to me it is not a practical objection, and even if it is made out that there is a scientific and theoretical action on the flour which may be said to be deleterious, there is no evidence that there is any practical substantial deleterious result of which I can take account."

That really is the crux of the whole question, and those interested in public health will have to see in the future that the scientific objection never becomes substantial and practical, just as some of our public authorities are attempting to minimise the dust, smell, noise, and other discomforts that attend the use of motor-omnibuses. Knowing as we now do the possible dangers which might ensue were millers allowed a free hand, it is necessary that if bleaching is still countenanced a strict watch should be exercised to keep its use within the limits of safety.

Beri-beri.

Here we pass from one of the important questions of the West to a somewhat similar problem which is mainly of Eastern interest.

No hypothesis hitherto advanced with regard to the origin[8] of beri-beri (the kakkee of Japan) has up till now found sufficient experimental confirmation to warrant its general acceptance. This applies equally to the conception of the disease as due to the presence of bacteria or other parasites, to toxins in the body or in food, or to "miasms." One fact, however, stands out clearly, and is now generally admitted by investigators, namely, that there is some connexion between the disease and rice. In all those Eastern countries in which the disease is endemic, every sufferer from beri-beri is a rice-eater, and conversely European residents who eat little or no rice do not get beri-beri.

During the Russo-Japanese war, very striking illustrations of the part played by rice in the causation of the disease came to light. I take one only. During the siege of Port Arthur, the Japanese army and navy lived under exactly the same conditions with one exception; in the army the old rice diet was still maintained, but in the navy a reform had been introduced by adding to the rice a certain amount of either meat or barley. The disease still continued to decimate the soldiers, but the sailors escaped almost scot-free.

The rice consumed in Japan is mainly "white rice," that is, rice freed from pericarp and husk, and finally polished.

A few years ago Dr. S. Kajiura, an officer of the Japanese Navy, worked in my laboratory, and undertook some experiments on beri-beri, or at least on a very similar disease with characteristic neuritis and nerve degeneration, which can be artificially produced in fowls. These are naturally not the first experiments performed in this way, but exception has been taken to the results previously published, because they were obtained in a possibly "infected" locality. Whatever objections there may be to King's College, it has the advantage of being free from any suspicion of harbouring beri-beri surreptitiously. The fowls fed on the white rice died within a few weeks with the usual symptoms and post-mortem appearance of beri-beri.[69] Kajiura in conjunction with Rosenheim had previously made a study of the nature of the proteins in rice,[70] a cereal which, curiously enough, had escaped any previous examination of the same kind; among the most noteworthy of their findings they ascertained that rice almost completely lacks a protein soluble in alcohol, similar to the gliadin of wheat and rye, or the hordein of barley. Thinking possibly that the absence of this protein might explain the harmful effect of an exclusive rice diet, they fed some of the birds on rice + hordein, and rice + gluten; other animals had added to their diet calcium carbonate and calcium phosphate in order to test the hypothesis advanced by others that lack of calcium or of phosphorus might be at the root of the matter. But in no case did they succeed in appreciably delaying the onset of death. Fowls fed on barley, however, showed no signs of the disease. The experiments were not sufficiently numerous perhaps, for Dr. Kajiura had to return to Tokio, but so far as they went they negatived the suggestion that the lack of a gliadin in rice is responsible for the production of beri-beri.

With the small space still at my disposal, I cannot attempt a review of the huge literature that has now centred around what is a national question for the Japanese. This will be found in certain publications issued during the year by the Japanese Government.[71]

I shall only deal, and that briefly, with three papers. The first

[69] Kajiura and Rosenheim, *J. Hygiene*, 1910, **10**, 49; *A.*, 1910, ii, 635. This paper contains numerous references to other authors.

[70] *Proc. physiol. Soc.*, 1908, liv; *J. Physiol.*, **36**; *A.*, 1908, ii, 317. The full paper will be published in the *Bio-Chem. J.*

[71] "Mitteilungen der Beri-Beri-Studien Kommission," Tokyo, 1911. "Sanitätsstatistik der Japanischen Armee mit besonderer Berücksichtigung der Beri-Beri in derselben," Tokyo. "Kriegsministerium," 1911. "Japan und seine Gesundheitspflege," by Rintaro Mori, Tokyo, 1911. The last-named book treats of many other subjects in addition to beri-beri and is a most interesting work on Japanese history.

of these deals with analyses of rice, and the economic value of rice in the tropics; it is only indirectly related to the subject we are discussing, and an abstract has already appeared in our Journal.[72] The second merits longer notice, because it does, I think, bring us nearer to the solution of the question, and is written by two of our own countrymen working in the Malay States.[73] They find that it is the removal of the "polishings" of the rice that produces the harmful effects. The natives of the Malay peninsula who consume unpolished or slightly polished rice do not suffer from beri-beri, but those who take polished rice do. Fowls fed on polished rice develop a form of polyneuritis analogous to beri-beri, whereas those fed on unpolished rice remain healthy. If the polishings removed from the rice are added to polished rice, fowls fed on the mixture also remain healthy. The harmful influence of white rice is not due to a poison developed in it after milling, but to the removal of some substance of high physiological importance essential to the maintenance of health.

The estimation of total phosphorus in any given rice indicates the extent of the milling or polishing to which it has been subjected, and therefore of its power in producing disease. The polishings are much richer in phosphorus than the part of the grain left behind. Rice containing 0·4 per cent. or more of P_2O_5 is safe.

The essential substance or substances are still unknown; they are probably small in amount, but whether they act by rendering other constituents of the diet available for nutrition, or whether they are themselves the nutritive material necessary for nerve-tissues is at present a matter of conjecture. The polishings are not only richer in phosphorised constituents, but are somewhat richer in the alcohol-soluble protein than the polished rice. The protective substances, as they may be termed, are destroyed by heating the unpolished rice to 120°. The fats contained in the peripheral layers of the grain are of no value as a protection against polyneuritis. The protective substances are soluble in 0·3 per cent. hydrochloric acid, but phytin, which comprises 32·5 per cent. of the substances so soluble, is without value as a protective. The protective substances are soluble in 91 per cent. acidulated alcohol, and exclusive of dextrose amount to not more than 11 per cent. of the polishings, and not more than 1 per cent. of the original grains. In this fraction the alcohol-soluble protein

[72] Aron and Hocson, *Biochem. Zeitsch.*, 1911, **32**, 189; *A.*, ii, 625.

[73] "Studies from the Institute for Medical Research, Federated Malay States," No. 12. "The Etiology of Beri-Beri," by Henry Fraser and A. T. Stanton. Singapore, 1911. 89 pages.

and compounds of calcium, magnesium, and phosphorus are included.

This narrows down the search very considerably, and one hopes that it may not be long before the protective substance is fully identified, although one is naturally cautious in prophesying; such materials one knows by experience are often very elusive.

The third and last paper to which I have to refer has been published since the foregoing paragraphs were written, and contains an important fulfilment of the hope just expressed.[74] Funk shows that the protective substance present in the polishings and absent from polished rice is present only in minute amount, probably not more than 0·1 gram per kilo. of rice. It is an organic base, and a crystalline nitrate was prepared from it, of which an elementary analysis was made. The figures are, however, given with caution, as the supply of material was too small for duplicate analyses. The curative dose of this material was found to be extremely small.

If there is any value in arguing from analogy, it is quite possible that the outer portions of the wheat grain may also contain some material of special importance.

W. D. Halliburton.

[74] "The Chemical Nature of the Substance which Cures Polyneuritis in Birds induced by a Diet of Polished Rice." By Casimir Funk. *J. Physiol.*, 1911, **43**, 395.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

The year 1911 has not been made noteworthy by the publication of any paper of special value; nothing has appeared that can be claimed as a new discovery, or that would indicate a fresh point of view or a novel method of attack on the many complicated problems with which the agriculturist has to deal. It is, however, perhaps permissible to note that a steadily increasing volume of sound scientific work is being turned out by British investigators. The agricultural colleges and departments are all occupying themselves in research, and the quality of the work turned out shows a distinct advance from year to year. Were no other evidence forthcoming, this might be seen in the style of the papers and the discussions on agricultural topics at the Portsmouth meeting of the British Association, which has now accorded the dignity of a full section to the subject of Agriculture. Attention may also be called to the fact that the Board of Agriculture has published the outlines of a scheme for the furtherance of agricultural research, which it is about to set in operation by the aid of funds provided by the Development Commission. According to this scheme the sum of £50,000 per annum is to be devoted to the prosecution of agricultural research, and it is proposed to establish for each of the main divisions of the subject—animal nutrition, investigation of the soil, plant chemistry and physiology, plant breeding, animal zoology, dairying, fruit growing, etc.—an institute to be attached to some existing university or agricultural college, which will be sufficiently subsidised to permit of the continued investigation of the fundamental problems involved, irrespective of their immediate translation into practice. The scheme further makes provision for grants to individual workers not necessarily connected with the institutes, after the manner of the grants for scientific research administered by the Royal Society, and also for the strengthening of the scientific staffs of the existing agricultural colleges to enable them to undertake local investigations and to give advice to the agriculturists within their sphere of action. With this aid it may be hoped that

as the scheme gets into operation the United Kingdom will develop a body of scientific workers comparable with those of other countries and worthy of the position which agriculture still holds in the national economy.

Soils.

During the year has been published the first attempt at a systematic soil survey of a portion of the British Isles, in the shape of a report on the agriculture and soils of Kent, Surrey, and Sussex by A. D. Hall and E. J. Russell.[1] These authors have taken the geological formations that are developed in that district as the basis of their work, and conclude that each formation gives rise to a soil type which can be characterised both by the mechanical analysis of the soils and by the special features in the farming prevailing over the out-crop. About sixteen different soils are dealt with, ranging from the Lower Wealden to the Bagshot Beds, together with three drift formations, and for each of these soils from ten to twenty analyses are given of samples taken from different parts of the area, both soil and subsoil being dealt with, and mechanical as well as chemical analyses reported. The authors find that the mechanical analysis alone provides a satisfactory basis for classification. The chemical analyses have all too much in common, and are too largely determined by the scheme of cultivation under which the soil has been worked, although certain correlations are shown to exist between some features of the mechanical and the chemical analyses, especially as regards the proportions of alumina and potash. On the basis of the analyses and of the authors' acquaintance with farming practices in the district, recommendations are made as to the systems of manuring, etc., appropriate to each formation. The report also contains a series of maps showing the distribution of crops within the area, and in the text these are correlated with the character of the soils. Finally, the information derived from the occurrence of particular crops in different parts of the area is gathered together to lead to conclusions as to the nature and composition of the soil best suited to wheat, barley, fruit, hops, etc., under the climatic conditions prevailing, for it is shown that the variations of the rainfall have a considerable influence on the cropping best adapted to a particular type of soil. In a further article[2] the same authors discuss some of the more scientific questions on which the information accumulated in the report throws light. They give examples to

[1] "Agriculture and Soils of Kent, Surrey, and Sussex," published by the Board of Agriculture and Fisheries, H.M. Stationery Office, 1911.

[2] *J. Agric. Sci.*, 1911, **4**, 182.

show the agreement which may be expected between the analyses of samples taken in different places on the same soil type, and how these may be modified by local accidents which result in washing or flooding. They show again how other formations change in character progressively along or across the out-crop, owing to a change in the conditions under which the formation was originally deposited. They then proceed to discuss the interpretation of mechanical analyses and the relation they bear to climate and situation. Complete mineral analyses are given of the various fractions obtained by mechanical analyses, to illustrate the change of composition in passing from the coarser to the finer fractions. These analyses also indicate the existence of two distinct types in the material determined by the mechanical analyses as "clay"; in the more fertile soils the clay contains about 21 per cent. of alumina and more than 50 per cent. of silica, whereas the clay from a group of second-rate soils contained about 30 per cent. of alumina and less than 50 per cent. of silica. In the discussion of the chemical analyses it is shown how difficult it is to attach any significance to the absolute amount of plant food contained in the soil; for example, the nitrogen, which is generally about 3 per cent. of the loss of ignition, may be associated with a rich soil or with a soil in which the conditions are so unfavourable that organic matter does not decompose. It is shown that the amount of alumina soluble in hydrochloric acid is approximately equal to one-third of the clay fraction determined by mechanical analysis, and that the potash is commonly about one-tenth of the alumina, thus indicating that the hydrochloric acid must break down some definite group of silicates in the soil. A few soils show exceptions to this rule, all soils possessing a special character marked by an exceptional proportion of fine silt. No correlation was found between fertility and the lime-magnesium ratio, and the amounts of ferric oxide present were similarly non-significant. Manganese was determined in nearly all the soils, but no significance can be attached to the results.

Hall and Russell's work purports to be little more than a preliminary sketch, even for the district under examination, but it does indicate the lines on which such work can proceed and what returns of practical and scientific value may be expected from systematic soil analysis, the value of which will increase with each addition to the number of analyses and to the area over which they extend. It becomes obvious, for example, that little advice can be given to the farmer on the strength of an isolated soil analysis unless the result can be compared with those of the type to which the soil belongs. It is the departures from the type that are signi-

ficant, and may provide the clue to the solution of the difficulties which the farmer experiences with the soil.

O. Lemmermann and his colleagues in Berlin[3] report a number of vegetation experiments with soils showing various lime–magnesia ratios, but they have been unable to substantiate Loew's opinion that this ratio is of significance to the fertility of the soil, a conclusion which had also been reached by Hall and Russell in their survey mentioned above. Lemmermann also proceeded to compare the results given by analysis as to the amount of lime and magnesia in the soil with the response of the same soils to dressings of these substances in vegetation experiments. They obtained very inconclusive results wherever the amounts of lime were small; in other words, determinations of the amount of lime in the soil gave little or no indication of whether the soil was in need of lime or not. It should be noted, however, that these authors determined simply the lime soluble in dilute acid or in a solution of ammonium chloride, whereas it has been often pointed out that only the lime as carbonate in the soil can be of any significance in determining its fitness for plant nutrition, and that recourse must be had to one of the methods that will measure minimal amounts of carbon dioxide evolved from the soil without decomposing the organic matter, which in certain acid soils also gives rise to carbon dioxide under the action of acid. A somewhat similar question has been examined by H. R. Christensen and O. H. Larsen.[4] These authors examined more than one hundred soils, the need or otherwise of which for lime was known; they determined the carbon dioxide set free by acids, the amount of calcium dissolved by an ammonium chloride solution, the behaviour of the soil towards litmus, and, lastly, applied a biological test, in which 5 grams of the soil were introduced into 50 c.c. of 2 per cent. mannite solution and inoculated with *Azotobacter*. *Azotobacter* will only develop under these conditions when the soil contains calcium carbonate, and the results yielded by this test were found to agree with the known behaviour of the soil in 90 per cent. of the cases tested, whereas the litmus reaction failed to agree in 40 per cent. of the cases, the ammonium chloride method in about half the cases, whilst the determination of carbon dioxide failed more often than not to indicate correctly whether the soil was in need of lime.

O. Schreiner[5] and his colleagues, E. C. Shorey and E. C. Lathrop, in the Bureau of Soils of the United States Department of

[3] *Landw. Jahrbuch.*, 1911, **40**, 175, 255.

[4] *Centr. Bakt. Par.*, 1911, ii, **29**, 347.

[5] *J. Biol. Chem.*, 1910, **8**, 381; 1911, **9**, 9; *A.*, ii, 65, 327; *J. Amer. Chem. Soc.*, 1911, **33**, 1412; *A.*, ii, 923.

Agriculture have continued their investigation of the organic substances that can be isolated from soils, and have compiled a long list of substances isolated in a pure state. Amongst acid substances they have obtained hydroxystearic, dihydroxystearic, picolinecarboxylic, agroceric, paraffinic, and lignoceric acids. Amongst protein cleavage products they find arginine, histidine, cytosine, xanthine, hypoxanthine, whilst C. S. Robinson[6] has isolated leucine and *iso*leucine; other substances identified are phytosterol, agrosterol, coumarin, and similar substances. All of these may be supposed to be derived from the decomposition of plant residues by bacterial actions, and the authors appear to be abandoning the idea that was once put forward that they are direct excretions from the plant's roots. Schreiner, however, still regards many of them as direct causes of unfertility; for example, he finds that the presence of dihydroxystearic acid almost invariably accompanies infertility in soils and is associated with conditions of poor drainage, lack of lime, and deficient aeration. Again he finds[7] that some of these substances have specific effects on plants; coumarin, for example, causes a peculiar distortion in the leaves of plants when it is added to the nutrient solution in which they are growing. Vanillin inhibits the development of roots, whilst *p*-benzoquinone induces a specially tall and slender growth. These effects can be inhibited by particular fertilisers; for example, the presence of phosphates prevents coumarin from taking effect, the vanillin action is overcome by nitrates, and that of *p*-benzoquinone by potassium salts. Whilst such results, if they can be confirmed and extended from growths in water cultures to soils, would lend support to the theories of fertiliser actions which are associated with the American Bureau of Soils, they seem slender evidence against the conception of the direct nutritive action of fertilising substances. R. G. Smith[8] has also examined soils for toxic substances, and he has been able to extract from them a bactero-toxin soluble in water and filterable through porcelain, which inhibits the growth of bacteria. This substance is destroyed by heating, sunlight, or storage, and its existence in soils might be appealed to in order to explain some of the results obtained by Russell and Hutchinson and by Pickering. Russell and Hutchinson's original investigations, therefore, took into account the possibility of such an inhibiting substance, but showed by crucial experiments that its removal cannot be the factor causing the increase of fertility of soils after they have been heated or exposed to the

[6] *J. Amer. Chem. Soc.*, 1911, **33**, 564; *A.*, ii, 431.
[7] *Proc. Amer. Soc. Biol. Chem.*, 1910, xiii.
[8] *Proc. Linn. Soc., N.S. Wales*, 1910, **35**, 808.

vapour of antiseptics. R. G. Smith has also investigated the waxy and resinous substances which can be extracted from soils, and finds that they may form a waxy coating on the soil particles which causes them to be less readily attacked by water and bacteria. The possibility that the accumulation of material of this kind in soils which have been long under cultivation and heavily dressed with organic manures, might cause the characteristic difficulty in wetting such so called worn out soils when dry, has been considered by other observers, but it has never yet been demonstrated that the removal of such material by ether, etc., causes any difference in the manner in which water will move in the soil.

Amongst other investigators of the organic constituents of the soil may be mentioned A. G. Dojarenko,[9] who has investigated the products of the oxidation of humic acid with hydrogen peroxide. He finds that compounds containing nitrogen as amide and amino-acid pass into oxidised forms of humic acid, such as apocrenic acid, whilst the humin-nitrogen is transformed into simple amides and ammonia. Dojarenko suggests that this method may serve to discriminate between the nitrogen in the soil which is stable and that which is likely to become available for plant nutrition when the organic matter is oxidised.

Several investigations are reported on the colloid substances in the soil and the part they may be supposed to play in its behaviour towards water and fertilisers, but nothing very definite has yet emerged, and the results are hardly suitable for abstraction. J. König [10] and his co-workers describe a method for the estimation of this colloid matter by determining the amount of methyl-violet which a given weight of the soil can withdraw from solutions of 1, 2, or 3 per cent. strength, according to the character of the soil. The method has not yet received sufficient trial to determine its practical value, but it is one of easy application, and as it promises to afford a simple measure of one of the most important factors in the physics of the soil—the extent of the active surface of the particles which is very imperfectly gauged by methods of mechanical analysis, it may be recommended for further examination to anyone who is engaged on the analysis of a large number of soils. In the domain of soil physics an interesting paper has appeared by W. H. Green and J. A. Ampt,[11] in which they describe a simple form of apparatus for determining the permeability and capillary constants of soil, on which both the movements of air and water through soil depend. The apparatus is such as can be readily fitted up and

[9] *7th Int. Congr. App. Chem.*, 1909, VII, 11; *A.*, i, 357.
[10] *Landw. Versuchs. Stat.*, 1911, **75**, 377; *A.*, ii, 1033.
[11] *J. Agric. Sci.*, 1911, **4**, 1.

manipulated in an agricultural laboratory, and it is now necessary to ascertain if the constants thus determinable will prove of practical value in interpreting the behaviour of soils when a large number of soils of varied types come to be examined.

Soil Bacteriology.

Although a very large number of papers have been published on this subject, nothing very striking or suggestive has arisen during the year; in fact, most of the papers rather leave a feeling of volume and diffuseness than of clear conclusions that can be adapted to the interpretation of soil conditions in nature. Whilst it is easy to trace the great changes that are being brought about by bacteria in the soil, as, for example, the mobilisation of the nitrogen reserves and the preparation of them for the higher plants, it is difficult to bring these changes with their mutual inaction within the sphere of quantitative measurement. The methods which have been so far devised for measuring the power of the soil to effect any particular type of change seem to be vitiated by the entirely artificial conditions under which the soil is placed in the laboratory, and the great desideratum at present is a system of measuring the activity of the soil in a manner that will agree with results obtained in situ. As to the general bacterial activity in the soil, R. Emmerich and his colleagues [12] have described certain experiments in which the addition of starch at the rate of 0·6 per cent. to a loamy soil brought about a considerable retardation of growth, the roots of the test plants turned brown and to a large extent died off. This injurious action is attributed to the enhanced bacterial activity in the soil brought about by the condition of the carbohydrates. An excessive number of bacteria acts harmfully on the roots by withdrawing oxygen and so depressing their powers of assimilation, and also by the formation of hydrogen sulphide in the de-oxygenated atmosphere of the soil through the reduction of sulphates by the bacteria. The roots, in fact, become choked because they cannot compete with the bacteria for the restricted air supply. H. B. Hutchinson and F. S. Marr [13] report some similar but earlier experiments, in which the application of starch and sucrose to the soil of certain of the Rothamsted experimental plots resulted in a marked reduction of the yield. Examination of the soil after the application of the carbohydrate showed a great increase in a number of bacteria and moulds there present; in one case the bacteria increased in number after the treatment from about 6·4 to 14·9 millions per gram of soil. Certain experiments in pots confirmed

[12] *Centr. Bakt. Par.*, 1911, ii, **29**, 668; *A.*, ii, 430.
[13] *7th Int. Cong. App. Chem.*, 1909, VII, 37; *A.*, ii, 430.

these trials in the open. Such results would seem to contradict the hypothesis that an increase of nitrogen in the soil will follow a supply of carbohydrate because of the activities of nitrogen-fixing organisms like *Azotobacter*. The action of *Azotobacter* is normally limited in soils by the lack of carbohydrate, from the combustion of which the *Azotobacter* derives the energy necessary to bring the nitrogen into combination. The explanation of these anomalous results has since been found in the fact that the carbohydrate was supplied to the soil in the spring at the time when it is at such a low temperature that other bacteria, for example, some of the simple putrefactives, are far more active than *Azotobacter*. In later experiments the carbohydrates, starch or sugar, have been supplied to the same plots in the autumn directly after the removal of the crop; the soil is then warm, *Azotobacter* is active and can utilise the carbohydrate, with the result that sufficient nitrogen is fixed to produce an undoubted increase of crop in the following season.

The action of the nitrogen-fixing organisms, and particularly *Azotobacter*, continues to be the subject of investigation. One of the points that has hitherto been somewhat difficult to understand is the comparatively high rate of fixation which some of the field results would appear to indicate, as compared with the small amounts of nitrogen obtained in a combined state in laboratory experiments, in which 10 milligrams of nitrogen fixed for each gram of carbohydrate destroyed are rarely exceeded.

A. Koch and S. Seydel[14] have investigated this question in a somewhat novel fashion, in that after the infection of a dextrose solution with *Azotobacter* they determined from day to day the amount of nitrogen fixed and also the amount of dextrose that had been oxidised. Under these conditions they found that in the earlier days there is a very much higher ratio between the amount of nitrogen already fixed and the dextrose oxidised, as high, in fact, as 50 or 60 mgm. of nitrogen per gram of dextrose. The authors attribute the falling off in the later stages of fixation to the accumulation of nitrogenous material in the medium, whereupon the organism begins to employ the carbohydrate for other purposes than fixation. In the open ground this accumulation and concentration of nitrogenous material by the *Azotobacter* itself is not likely to occur, so that they consider that the organism will continue fixing nitrogen at the higher ratios indicated in the earlier stages of their experiment.

T. Remy and G. Rösing[15] have also investigated the reasons for the greater effectiveness of *Azotobacter* in soils than under labora-

[14] *Centr. Bakt. Par.*, 1911, ii, **31**, 570. [15] *Ibid.*, **30**, 349; *A.*, ii, 758.

tory conditions, and they find that with cultures in soil extracts the presence of humus stimulates the action of *Azotobacter*. This stimulus they attribute to the small quantities of iron and similar silicates that the humus contains. They also found that the value of ferric iron for the development of *Azotobacter* very much depends on the form of combination in which it is supplied. Ferric hydroxide dissolved in sucrose is perhaps the most effective form, but ferric silicates are also valuable. It is to the presence of soluble substances of the latter class in basic slag that they are disposed to attribute some of the very beneficial effects which basic slag has been noticed to have on the development of *Azotobacter* and the fixation of nitrogen.

Some very remarkable effects of *Azotobacter* are reported from Colorado. There W. P. Headden has previously indicated the existence of certain soils which develop sometimes in small patches and at others in considerable areas, and become absolutely sterile through the accumulation of salts and particularly of nitrates in the surface soil. In a bulletin[16] published during the year a detailed examination is given of twenty-two examples of such soils. The analyses are remarkable; the soil is always brown and mealy in texture, and contains an unprecedented amount of material soluble in water; for example, in one case the top foot contains as much as 1·127 per cent. of soluble material, of which 23 per cent. consisted of nitrates calculated as sodium nitrate. The top inch and a-half of this soil contains as much as 5·5 per cent. of material soluble in water, more than half being nitrates, and Headden calculates that an acre of the land down to the depth of 13·5 inches contains no less than 30 tons of nitrates, principally sodium nitrate. The author shows that the presence of these substances cannot be put down to surface water bringing nitrates from a distance and accumulating them by evaporation; in nearly all cases the land is reasonably elevated, the sterile spots being no lower than the surrounding country; it is well drained, and the water table never near the surface. The natural waters in the district do not contain any exceptional amount of nitrate, nor does the water used for irrigation. The brown spots develop in some cases with great suddenness, and the crops either grow very badly or not at all; established orchards which existed in most of the cases examined are rapidly killed outright as soon as the brown patches appear. All the appearances indicate that the excessive amount of nitrate is the cause of death, as, for example, the intense green of the foliage, followed by scorching at the edge and tips of the leaves, and the author was able to reproduce the

[16] *Agric. Exp. Sta., Colorado*, 1911, *Bull.* 178.

effects by the employment of excessive amounts of sodium nitrate. The origin of these large quantities of nitrates Headden sets down to the fixation of nitrogen by *Azotobacter* and its rapid nitrification afterwards, and he shows that laboratory samples of these soils when placed under favourable conditions of incubation fix exceptional amounts of nitrogen, as much as 10·5 milligrams per 100 grams of soil in twenty-seven days. W. G. Sackett [17] undertook the bacteriological study of the soils, and was able to establish the fact that they were able to fix nitrogen, when incubated in a damp condition and without any addition of carbohydrate, at a very exceptional rate, sufficient to account for the nitrates found in the soil, provided that nitrification kept pace with fixation. *Azotobacter chroococcum* was the dominant nitrogen-fixing organism in the soil, and the brown colour so characteristic of the sterile patches was shown to be due to the pigment developed by this organism. When the nitrates accumulate to the exceptional extent indicated in some of the soils, fixation ceases, and the *Azotobacter* may even be killed off. Saturation of the soil with water also limits the fixation of nitrogen. These results are very remarkable, and so far as we are aware have not been paralleled anywhere else. The point that is not yet clear is whence the *Azotobacter* derives the energy necessary to bring such quantities of nitrogen into combination, but the prime fact that in these soils sterility is due to an excess of nitrogen and particularly of nitrates, seems to be fully established, an extraordinary result when we remember that under ordinary conditions of agriculture all over the world the difficulty is to obtain sufficient nitrogen and nitrate to get the soil up to its maximum fertility.

H. Pringsheim [18] has added to the number of bacteria which are known to fix nitrogen by isolating from ordinary garden soil certain thermophilic organisms which fix from 3 to 6 milligrams of nitrogen per gram of dextrose destroyed. The soil is incubated with a Winogradsky solution containing a little soil extract at a temperature of 61°, whereupon only a few bacteria proved to be capable of development at this temperature, and these fix nitrogen in the manner indicated.

No particularly novel work in connexion with the beneficial effects of heating and partial sterilisation of the soil is reported this year, although several investigators have published papers of the effects of carbon disulphide, ether, and similar substances on the bacterial content of the soil. They generally ignore the issue that has been so definitely raised by Russell and Hutchinson, and

[17] *Agric. Exp. Sta., Colorado*, 1911, *Bull.* 179.
[18] *Centr. Bakt. Par.*, 1911, ii, **31**, 23 ; *A.*, ii, 916.

fall back on the hypothesis of stimulus by the antiseptic to the organism, although Russell and Hutchinson described critical experiments which put such explanations out of court.

T. Goodey,[19] working at Rothamsted, has published descriptions of the various protozoa to be found in cultivated soils, and also recounts a method for driving these organisms out of the soil and enumerating them without having to go through the process of cultivation. This method is valuable, because it is rarely possible to pick up the organisms by a microscopic examination of the soil itself, still less to enumerate them. Goodey's paper goes on to adduce evidence that the ciliated organisms, at any rate, must be in an encysted condition in the soil under normal conditions, and therefore incapable of carrying out the function of limiting the number of bacteria with which they were credited by Russell and Hutchinson. There still remain other organisms like amœba, to which this objection does not apply, but in all probability the bacteria themselves are functioning but slowly in the soils as examined by Goodey; hence the two sets of organisms come into activity simultaneously when the conditions of moisture and temperature are favourable, and the ciliated protozoa may still play their part of limiting bacterial activity in the soil.

E. J. Russell and J. Golding[20] have issued a first report on the bearings of the protozoa theory on sewage-sick soils. They find that the soils on land which has been over-watered with sewage are swarming with protozoa, but possess to a very limited degree the bacterial activity by which the purification of the sewage should be effected. Treatment with lime had no beneficial effect on such soils, but a partial charring of the surface soil or treatment with various antiseptics restored at once its power of purifying the sewage. Coincident with this came an enormous increase of the number of bacteria present in the soil; for example, in one case the sewage-sick soil contained only 40 million bacteria per gram, but after treatment and when the land was again functioning in the purification of sewage, the numbers rose to 400 million per gram.

S. Suzuki[21] and A. J. Lebedeff[22] have continued the very interesting studies initiated by Beyerinck on the production of gaseous nitrous and nitric oxides from nitrates by various reducing organisms, and have added to our knowledge the conditions under which one or other of these gases are produced. Suzuki obtained only nitrous oxide with the materials that he examined, whereas Lebedeff

[19] *Proc. Roy. Soc.*, 1911, B, **84**, 165.
[20] *J. Soc. Chem. Ind.*, 1911, **30**, 471.
[21] *Cent. Bakt. Par.*, 1911, ii, **31**, 27; *A.*, ii, 916.
[22] *Ber. Deut. bot. Ges.*, 1911, **29**, 327; *A.*, ii, 917.

obtained abundant nitric oxide, sufficient in some cases to give brown fumes when the gas evolved came in contact with the air.

M. C. Potter [23] describes a very interesting set of experiments in which the disintegration of organic compounds by micro-organisms becomes a source of electrical energy. A special form of cell was constructed, in which one platinum electrode was in contact with a nutritive solution, for example, dextrose, and the other in contact with the same nutritive solution containing also an organism such as yeast. A difference of potential was at once established, of the order of from 0·3 to 0·5 volt, and the electrical activity was parallel to the activity of the yeast as measured by the carbon dioxide evolved.

C. T. Gimingham [24] has published an investigation into the formation of calcium carbonate through the oxidation of calcium oxalate in plant residues by soil bacteria. It had previously been shown that oxalates are capable of further oxidation to carbonates by the bacteria contained in soil, and Gimingham attempted to obtain pure cultures of the organisms. There is no difficulty in bringing about the change by a crude culture obtained by inoculating a little garden soil into an aqueous extract of soil to which calcium oxalate has been added, but the isolation of the organisms presented some difficulty, as also attempts to induce pure cultures of various oxidising bacteria to attack the salt. In the end it was found necessary to develop a strong active culture of the organism in a medium containing very little organic carbon, as the organisms only attack the carbonate when they have exhausted the more available organic matter. Some of these organisms were isolated by dilution methods, and each of them, when heavily inoculated into a flask containing sterile soil extract and calcium oxalate in suspension, produced after a time crystals of calcium carbonate on the walls of the flask. The organisms are all aerobic, but in view of the number that were found capable of effecting the change, specific differentiation did not appear to be necessary. A number of well known organisms were also examined in a pure state, none of which, except *Azotobacter*, could oxidise the oxalate.

Chemistry of the Growing Plant.

The mechanism of assimilation continues to attract the greatest amount of attention. As to the actual chemistry of the process by which carbon dioxide and water are transformed into sugars and

[23] *Proc. Roy. Soc.*, 1911, B, **84**, 269 ; *A.*, ii, 913.
[24] *J. Agric. Sci.*, 1911, **4**, 145.

oxygen, J. Stoklasa and W. Zdobnický[25] obtained a sugar by the action of nascent hydrogen on carbon dioxide in ultra-violet light. In the presence of potassium hydroxide formaldehyde was produced, and the action did not proceed without the ultra-violet rays. The nature of the sugar was not determined, but a crystalline osazone was obtained, melting at 196—200°. G. Inghilleri[26] sealed up a tube containing a 40 per cent. solution of formaldehyde with crystalline oxalic acid, and exposed it to sunlight for fourteen months, at the end of which period he obtained a crystalline carbohydrate, which was optically inactive and was assumed from its physical properties to be sorbose.

One of the most important questions connected with assimilation within the green leaf itself is the order in which the different carbohydrates are produced. In most plants starch is the product of the action of light most readily recognised, but Brown and Morris some years ago brought evidence to show that sucrose is the first visible product of the assimilation process, and that the starch results from a secondary transformation in the leaf. The starch is further removed during the absence of light and accumulated in some other part of the plant in various forms—sucrose, starch, inulin, etc. The plant must be regarded as capable of bringing about a number of enzymic transformations that can as yet hardly be paralleled in the laboratory. Moreover, the leaves of many plants show the presence of dextrose, lævulose, and maltose, and the question arises whether these sugars are to be regarded as down-grade products of the sucrose and starch first formed, or whether they are up-grade products preceding the formation of the more complex carbohydrates.

J. Parkin[27] has examined the question afresh, working with the leaves of the snowdrop, which contain no starch although both starch and inulin are stored in the bulb. In the leaves of the snowdrop he found only sucrose, dextrose, and lævulose, maltose being absent, and the total sugars may amount to as much as 30 per cent. of the dry weight of the leaf. During the early part of the season there is more sucrose in proportion to reducing sugars in the leaf than later, but during any single day the percentage of reducing sugar remains fairly constant, although the sucrose increases during the day and diminishes during the night. As a rule, the lævulose is present in excess of the glucose. Parkin considers that his result supports Brown and Morris' theory that sucrose is the first recognisable carbohydrate to appear in the leaf,

[25] *Biochem. Zeitsch.*, 1911, **40**, 433; *A.*, i, 178.
[26] *Zeitsch. physiol. Chem.*, 1911, **71**, 105; *A.*, i, 354.
[27] *Biochem. J.*, 1911, **6**, 1; *A.*, ii, 1127.

and that the hexose sugars arise from it by hydrolysis precedent to translocation, although the results are not contradictory of the hypothesis that the hexose sugars are first formed. Parkin points out that Strakosch in 1907, working by microchemical methods, was able to recognise dextrose only in the mesophyll, the lævulose and sucrose only occurring in the veins and still more in the midrib and petiole. Sugar determinations in the cut-out tissue supported the view that dextrose is the first sugar to be formed by photosynthesis and then travels from the mesophyll to the small veins, where it is in part transformed into lævulose. The two hexoses then combine to produce sucrose, in which form the carbohydrate travels to the storage organs. Certain determinations, as yet unpublished, on the fluctuation of the carbohydrates of the leaf taken at two-hourly periods during the day and night would rather agree with Strakosch's theory, indicating that the first effect of light is a slight rise in the proportion of reducing sugars which remain constant at this somewhat higher level during the whole daylight; the rise in sucrose occurs a little later, and in its turn is followed by a continuous rise in the proportion of starch as long as the daylight lasts. The maltose, on the contrary, reaches its maximum during the night and its minimum during daylight, thus indicating that maltose is a down-grade product from the starch, which would agree with Parkin's failure to find maltose in the snowdrop leaf, where starch is also absent. More numerous and exact data are certainly wanted, especially as the quantitative discrimination of the sugars in leaf tissue presents a number of experimental difficulties, but the question is an important one, because until it can be decided which sugar is the first product of photosynthesis, it is difficult to speculate as to whether the earlier stages begin with the formation of formaldehyde or not.

R. Willstätter[28] and his colleagues have continued their important studies of chlorophyll and its derivatives, and have revised some of their earlier conclusions. They find that crystallised chlorophyll contains one ethoxy- and one methoxy-group, not two methoxy-groups as before stated, and that amorphous chlorophyll contains one methoxy- and one phytyl group. The figures previously given for the proportion of amorphous chlorophyll in the leaf are too low, because during the extraction of the leaf enzyme actions convert the amorphous into the crystalline chlorophyll if the process of extraction is at all slow. The change is due to a specific enzyme, chlorophyllase, which belongs to the group of esterases and can be extracted separately from the leaf. Willstätter describes methods of rapid extractions of the leaf which yield a much higher product

[28] *Annalen*, 1910, **378**, 1, 18, 73; 1911, **380**, 148, 154, 177; *A.*, i, 140, 659.

of amorphous chlorophyll than before. Willstätter further describes the relationship of chlorophyll to its derivatives. The fundamental acid from which they are all derived is a tricarboxylic acid of the formula $C_{31}H_{29}N_4Mg(CO_2H)_3$, which he terms chlorophyllin. The monomethyl ester obtained by hydrolysis of chlorophyll he calls chlorophyllide; then amorphous chlorophyll is phytyl chlorophyllide, and crystalline chlorophyll is ethyl chlorophyllide. The synthesis of chlorophyll from chlorophyllide and phytol can be effected by the enzyme above mentioned, but the yields are small. Other papers deal with the derivatives of chlorophyll, including those which contain no magnesium.

Further progress has been made of the study of the remarkable changes brought about by chloroform, toluene, and similar substances on the living tissues of the plant. In continuation of their former work, H. E. and E. F. Armstrong[29] show that the leaves of *Aucuba japonica* when exposed to the action of volatile organic vapours such as toluene, chloroform, or ether, become rapidly a rich chocolate-brown and ultimately black. The action of the excitant—the hormone as the authors term it—is to liberate the enzymes of the cell, whereupon glucosides are hydrolysed and oxydases are rendered active, the blackening of the leaf tissue being in all probability an oxidising action. Acid solutions and most salts are incapable of starting this action in the leaf, but mercuric chloride, cadmium iodide, sodium and potassium fluorides, carbon dioxide, hydrogen sulphide, and ammonia penetrate the leaf and initiate the changes. In a later paper the authors point out that the translocation of substances like sugars in the plant is periodically taking place at some times and not at others, and that therefore the cell wall must be alternately permeable and impermeable. This change in the permeability in the cell wall might be brought about by the action of hormones. In particular they show that the *Aucuba* leaf when exposed in water containing one of the hormones allows reducing sugar to pass out from the leaf into the water, although if placed in pure water no such diffusion of the sugar takes place. If the hormone used is hydrogen cyanide, the changes within the leaf take place, but no sugar passes out, which seems to show that the different hormones are not alike in their action on the differential septa of the living tissue.

A further very interesting series of observations in this subject have been published by I. Giglioli,[30] who attributes the action of the chloroform and other vapours, among which he particularly

[29] *Ann. of Botany*, 1911, **25**, 507; *A.*, ii, 642; *Proc. Roy. Soc.*, 1911, B, **84**, 226; *A.*, ii, 918.

[30] *Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 349; *A*, 1912, ii, 79.

instances the essential oils of the various aromatic plants, to the changes which these vapours bring about in the surface tension of water. He took sand and various soils saturated with water and drained them until they yielded no further water, then exposed them to the vapours in question. The sand or soil immediately parted with more water; for example, in one case with coarse sand as much as 31 per cent. of the water that was previously retained exuded from it under the action of chloroform vapour. With soils proper the exudation was not so great because of the imperfect penetration of the vapour into the homogeneous soil. The same exudation of water took place from vegetable tissues; for instance, two thick fleshy leaves of the *Cactus opuntea* were placed separately in a moist atmosphere, one being exposed also to the vapour of chloroform. In twenty-one days the chloroformed leaf lost 23 per cent. of its weight in liquid which transuded from the whole surface of the leaf, whereas the non-chloroformed leaf lost less than 4 per cent. Moreover, as in the Armstrongs' experiments, a considerable amount of soluble material passed out with the transuding liquid from the chloroformed leaf, amounting at the end of the experiment to 20 per cent. of the dry weight of the leaf, whereas the transuding liquid from the non-chloroformed leaf contained only an insignificant proportion of soluble material.

Giglioli extended these observations to yeast, and showed that ordinary dry yeast when exposed to the vapour of chloroform, eucalyptus oil, and other volatile oils, rapidly softened and lost its structure until a quantity of clear liquid could be filtered off from it. This liquid was a solution of the enzymes of the yeast, and proved to contain both zymase and invertase, so that it would induce an alcoholic fermentation in solutions of sucrose or dextrose. Giglioli suggests that this may prove the readiest method of obtaining zymase from yeast. It is evident that the action of the volatile oils which many plants excrete must exercise some profound regulative effect on the movements of water and of translocating substances within the plant, but until more data accumulate it is difficult to speculate on the exact nature of the function. It is at any rate significant that the most highly odorous plants are generally those growing in dry, arid situations, and again that with many plants there is a sudden and considerable liberation of volatile oil with the advent of evening and the failing of the light.

The part played by excitants in starting some of the prime physiological changes in the plant is further illustrated by some experiments reported by P. Mazé.[31] He finds that if seeds of maize and peas are taken from the plants in an unripe condition, when

[31] *Compt. rend.*, 1910, **151**, 1383; *A.*, ii, 141.

they still contain from 50 to 60 per cent. of water, they cannot be made to germinate under sterile conditions, although they will sometimes do so in ordinary soil; whereas if the seeds are dried, germination will take place. Mazé finds the unripe seeds contain a small amount of acetaldehyde which inhibits germination, this material being removed by the drying process or by the action of certain bacteria and micro-fungi associated with the soil. The question of possible excretion from the plant root is still a matter of controversy, and G. André [32] has attacked it afresh by making estimations of the total quantity of inorganic constituents contained in the experimental plants during different stages of the growth. His results lead him to the conclusion that by osmosis alone the plant never parts with any of its salts, either from the dead leaves or by excretions from the roots. P. Mazé,[33] however, comes to almost exactly an opposite conclusion from experiments with maize, and concludes that both organic and inorganic salts are excreted from the roots and stomata.

It has been assumed that if a plant is supplied with an unlimited amount of the nutrient it requires in the food solution in contact with the roots, it is a matter of indifference what concentration the solution may possess. Such an assumption is, in fact, one of the bases of Whitney and Cameron's theory that all soils are sufficiently supplied with mineral plant food to satisfy the utmost requirements of the plant, and they quote certain old experiments where plants made complete growth in nutritive solutions of extreme dilution. I. Pouget and D. Chouchak [34] have grown seedlings in water cultures containing different amounts of phosphoric acid. In their experiments the assimulation of phosphoric acid by the plant was in direct proportion to the strength of the solution, when the concentration of phosphoric acid lay between 1·1 and 4 milligrams per litre. At lower concentrations, however, no such direct relationship was observed; both the growth and the amounts of phosphoric acid taken up were more irregular. Experiments of a similar nature have been made at Rothamsted, which tend to show that the concentration of the nutrient solution is a factor in the rate of growth in plants, even although the plant may be continuously bathed in a renewed solution of the nutrient, thus agreeing with the Russian investigators that plants cannot make their optimum growth when supplied only with an excessively dilute solution of nutrient, even although the total amount of plant food available may be in excess of the plant's requirements.

[32] *Compt. rend.*, 1910, **151**, 1378; *A.*, ii, 141.
[33] *Ibid.*, 1911, **152**, 452; *A.*, ii, 324.
[34] *J. Russ. Exp. Landw.*, 1910, **11**, 825.

H. B. Hutchinson and N. H. J. Miller[35] have continued their investigation of the compounds of nitrogen which can be utilised by the plant. Their experiments were made in water cultures under sterile conditions, and at the close the culture media were tested to make quite certain that no infection had taken place with bacteria which could break down the nitrogenous compounds. Despite the experimental difficulties attaching to such work, Hutchinson and Miller succeeded in growing a large number of plants which remained sterile until the end of the trial, and these proved to utilise a much larger range of nitrogen compounds than had hitherto been considered possible. Earlier experiments had demonstrated that ammonium salts can be freely taken up, and need not be first of all converted into nitrates. Of the compounds tested, carbamide was most freely utilised, then came barbituric acid, acetamide, alloxan, soluble humus, and peptone; then formamide, glycine, alanine, guanidine hydrochloride, cyanuric acid, oxamide, and hydroxylamine hydrochloride were utilised in small quantities, whereas ethyl nitrate, propyl nitrate, methyl carbonate, and also probably trimethylamine, *p*-urazine, and hexamethylenediamine gave negative results. Tetranitromethane proved to be toxic. Although in the soil, activity of the nitrifying bacteria is so great that the products of the bacterial attack on complex nitrogenous bodies are converted into nitrates before they reach the plant, it is yet evident that this final change is not necessary, and that the plant may, and, in fact, must in certain circumstances, derive its nitrogen from the less oxidised compounds formed at the earlier stages of the bacterial cleavage which is always going on in the soil.

Manures and Manuring.

An increased amount of attention is being given to the method of conducting field experiments; the limitations and the probable error attaching to the method are being considered in their bearing on the interpretation of the results obtained. With the great extensions of field trials, both of manures and varieties of crops, which have taken place during the last few years, and the contradictory results that are often reported with the most diverse explanations, it has often been felt that undue discredit was being brought on the value of such work, even when it only consisted in the demonstration of known principles, by the failure of the experimenter to recognise the magnitude of the error to which such work is subject, and the means by which such error can be reduced to a practical amount.

[35] *Centr. Bakt. Par.*, 1911, ii, **30**, 513; *A.*, ii, 920.

T. B. Wood and J. A. Stratton [36] have discussed their whole theory of the error attaching to determinations and experiments of an agricultural character, and show how the validity of the conclusions may be tested by statistical methods. They begin by showing how a series of analytical determinations of such inevitable variable material as is afforded by growing crops can be checked by the construction of frequency curves so as to ascertain whether the material is homogeneous and whether the mean result can be trusted to give the desired information. They further apply the method of least squares in order to obtain the probable error attaching to the mean result, and then proceed to discuss the results obtained by weighing up an apparently uniform acre of mangolds in plots each 1/1000th of an acre in area. The results would show that the probable error of a single plot amounts to about ± 5 per cent. of the total, and is not reduced by making the plot larger, so that the most accurate way of obtaining a valid result is to set out a number of similar plots of small size for each method of treatment adopted.

On similar lines W. B. Mercer and A. D. Hall [37] discussed the results obtained at Rothamsted by weighing up an acre of mangolds in 200 equal plots and an acre of wheat in 500 plots. The results were then combined to give the yield from larger plots of various sizes and shapes, and the probable error calculated in each case. Mercer and Hall find about the same probable error for a single plot as Wood and Stratton, but further show that the error diminishes with the size of the plot, although the reduction is small when the plot is larger than 1/40th of an acre. They also show that the error may be diminished by increasing the number of plots under similar conditions, provided the plots are scattered about the experimental area, although again the reduction in error is small when the number of plots is increased above five. They finally recommend that the unit of comparison in each experiment should be five plots, each of 1/40th of an acre and systematically distributed about the area under experiment. It is to be hoped that these papers will lead to an improvement in the method of conducting field experiments by the many local authorities who undertake this kind of work, so that the results accruing may possess some permanent value and be utilisable for further investigation.

As regards manures in general no very novel work is reported. The various fertilisers containing nitrogen obtained from the atmosphere continue to be tested, but the main principles of their action may be considered as settled except in the one case of artificial calcium nitrite, which, although not on the market in a

[36] *J. Agric. Sci.*, 1910, **3**, 417. [37] *Ibid.*, 1911, **4**, 107.

commercial form, might be produced in place of nitrate should it prove an equally valuable source of nitrogen. Various tests continue to be made with finely ground minerals containing phosphoric acid or potash, to ascertain if these substances can replace the present more expensive fertilisers which have been subjected to chemical treatment of some kind; for example, T. Remy [38] has compared finely ground raw Algerian phosphate with basic slag. In his experiments it gave but poor returns; its effectiveness was only about 5 to 10 per cent. of that of an equal amount of acid superphosphate, whereas basic slag had a comparative effectiveness of from 64 to 76 per cent. The returns from raw phosphates differ, however, with different crops; with blue lupins much the most favourable result was obtained. The use of finely ground phonolite has also been advocated as a source of potash in place of the Stassfurt salts, but in very few of the numerous results reported does this material yield to the plant any satisfactory amount of potash, and it is not likely to become a commercial fertiliser as long as the comparatively concentrated Stassfurt salts retain their present cheapness.

W. H. Hervey [39] reports a number of analyses of soot, a fertiliser in very common use in England, but likely to be variable in composition. The samples examined showed varying percentages, from 2·7 up to 5·5 of nitrogen, with exceptional cases of only 0·5 in the soot from a tall boiler shaft, and of as much as 11 per cent. in the soot from a kitchen chimney. Speaking generally, it was found that the content in nitrogen was higher the lower the weight per bushel of the soot. Practically the whole of the nitrogen in the soot consisted of ammonium salts.

A. D. Hall and N. H. J. Miller [40] report some further studies of the ammonia contained in the atmosphere. In their experiments dishes containing glycerol and water with a little sulphuric acid were exposed at various heights above arable and grass land for a period of two years, monthly determinations being made of the amount of ammonia absorbed. Care was taken to exclude flies and dust as thoroughly as possible, and under these conditions very much smaller results were obtained than those reported by other workers who have used similar methods. The dishes at higher levels always absorbed rather more ammonia than those near the ground, although this may be due to the better circulation of the upper air. The monthly absorption of ammonia was much the same in the winter and the summer months except near houses, where the winter results are definitely higher, probably owing to the con-

[38] *Landw. Jahrb.*, 1911, **40**, 559.
[39] *J. Agric. Sci.*, 1910, **3**, 398.
[40] *Ibid.*, 1911, **4**, 56; *A.*, ii, 763.

sumption of coal. The authors conclude that the method is not a satisfactory one for the study of the amount of ammonia contained in the atmosphere, nor do the results lead to a definite conclusion as to whether the soil is normally emitting or absorbing ammonia. They found, however, that a large increase in the ammonia absorbed close to the ground followed the application of ammonium salts as a fertiliser to the soil of the field above where the dishes were placed, hence a loss of ammonia is indicated from the soil to the atmosphere whenever the amount of free ammonium compounds in the soil becomes large.

The fungicidal action of the Bordeaux mixture is discussed in a paper by B. T. P. Barker and C. T. Gimingham,[41] who draw the conclusion that it is due to the action of solid precipitated copper compounds on the hyphæ of the parasite as they attempt to spread over the surface of the leaf, and not to any liberation of soluble copper compounds by the action of atmospheric carbon dioxide on the precipitated salt. In a further paper Gimingham controverts Pickering's idea that the value of Bordeaux mixture can be measured by the amount of soluble copper it will yield to carbon dioxide and water, because such a method postulates the action of pure carbon dioxide on the precipitate. The precipitated copper salts of Bordeaux mixture, whether basic sulphate or carbonate, do not yield any appreciable amount of soluble copper when exposed to the action of the atmosphere, because of the very low tension of carbon dioxide in such atmosphere. The amount of copper which passes into solution is, in fact, a function of the tension of the carbon dioxide with which the material is in contact, so that to submit the mixture to the action of pure carbon dioxide and water gives rise to misleading results.

Chemistry of Animal Nutrition.

This subject has suffered a severe loss during 1911 in the sudden and unexpected death of Oscar Kellner, which took place as he was attending the meeting of the Union of Agricultural Experiment Stations at Karlsruhe. Kellner's work at Möckern, which placed him at the head of the investigators of the nutrition of agricultural animals, his wide experience of agricultural conditions in various countries, and his powers of exposition, helped to render his ideas acceptable both to scientific and practical men. Kellner's chief contribution to the theory of animal nutrition is the conception of the starch equivalent, a single figure which sums up the value of the food to the animal from the energy point of view when all

[41] *J. Agric. Sci.*, 1911, **4**, 76.

deductions have been made both for the portions of the food that are not digestible and the energy which is spent by the animal in bringing about the digestion, and Kellner's careful experimental work succeeded in bringing into close agreement the experimental values of the starch equivalents of the foods examined and those deduced from its composition. Kellner had many friends in Great Britain, where his genial presence will be missed.

No very novel papers have appeared during the year, although F. Gowland Hopkins has described some yet unpublished work which promises to have considerable significance in the theory of nutrition. He has found that his experimental animals were unable to thrive on an unlimited artificial diet containing model proportions of pure proteins, fat, carbohydrates, and salts, and would even die on such a diet if persisted in. The addition of very minute traces, however, of various fresh extracts of animal or vegetable materials, milk, etc., to the diet enabled the animals to utilise it fully, although only an imperceptible increase in the amount of nutrient material as ordinarily measured was thus made. Now that the gross requirements of the animal in the way of energy and nitrogen supply have been established with a reasonable amount of accuracy, it is clear that the next step in estimating the practical value of different kinds of foods must be to obtain a knowledge of the small quantities of certain constituents overlooked in an ordinary analysis, but which by their action in stimulating certain physiological functions of the animal may be all-important to its power of utilising food.

Amongst other papers A. Morgen [42] and his colleagues at Hohenheim have re-investigated the effect on their food value of drying green fodders like grass. It is usually considered, on the strength of old experiments, that no change in the digestibility takes place, and that hay, for example, is as valuable a food as the grass from which it was made. These investigators find that such is not strictly the case; there is some slight loss of material during the drying process which may become large with bad methods of harvesting, and further, a slight falling off in digestibility, which is probably due to physical hardening of the tissues, necessitating an increase in the energy spent in digestion.

F. Tangl and A. Zaitschik [43] have examined the effect of watery foods on the secretion of milk, a question which has excited some interest in this country. They fed their test cows with green lucerne, beet, potatoes, marrows, etc., and reached a consumption of water in the food as high as 54 lbs. per diem per 1000 lbs. live weight. The animal, however, proved to be capable of regulating

[42] *Landw. Versuchs-stat.*, 1911, **75**, 321. [43] *Ibid.*, **74**, 183.

its milk secretion against such changes in the diet, and no variations in the composition of the milk followed the change from a comparatively dry to a watery diet. Their evidence is against the possibility that is often presupposed of adulterating the milk through the mouth of the cow.

In connexion with the chemistry of food-stuffs, F. W. Foreman[44] has hydrolysed the protein of linseed, a protein which, despite its importance in practical feeding, has hitherto escaped attention because of the difficulty of obtaining a pure product from the highly mucilaginous seed. The pure protein proved to contain 17·45 per cent. of nitrogen, and yielded, on hydrolysis, 1·03 of alanine, 12·71 per cent. of valine, 3·97 per cent. of leucine and *iso*leucine, 2·05 per cent. of proline, 4·14 per cent. of phenylalanine, 1·65 per cent. of aspartic acid, 11·55 per cent. of glutamic acid, 0·65 per cent. of tyrosine, 6·06 per cent. of arginine, 1·66 per cent. of histidine, 1·19 per cent. of lysine, and 1·94 per cent. of ammonia; glycine, serine, and tryptophan were also found. The exceptional feature about this analysis is the very high percentage of valine, of which not more than 2 or 3 per cent. has been obtained from other proteins.

M. Nierenstein[45] has investigated the nature of the nitrogenous compounds present in ripe cheese, and incidentally throws light on the claim often made that the ripening process results in the production of fat from the proteins of the cheese. Amongst the products of the ripening process of Cheddar cheese he finds cholesterol, cadaverine, putrescine, and aminovaleric acid, substances which are soluble in ether and account for the increased weight of the ether-soluble extract of the ripe cheese which has hitherto been regarded as fat. Making allowance for these substances, no evidence was found of fat-formation from protein in the ripening process.

Attention may be drawn to a very useful summary and discussion by H. P. Armsby[46] of a question to which allusion has frequently been made in these Reports, namely, that of the utilisation of the non-protein nitrogenous compounds of food—the amino-acids and amides—which of late years has been a subject of a considerable amount of investigation. Armsby points out very clearly that the experimental results obtained can be divided into two classes. With carnivora and herbivora these non-proteins are merely oxidised in the organism, and cannot in any way replace the proteins. With ruminants, however, the nitrogenous compounds are converted by

[44] *J. Agric. Sci.*, 1911, **3**, 358; *A.*, i, 341.
[45] *Proc. Roy. Soc.*, 1911, B, **83**, 301; *A.*, ii, 326.
[46] *U.S. Dept. Agric. Bureau Animal Ind.*, 1911, *Bull.* 139.

bacteria in the digestive tract into proteins, which afterwards become digested and may serve for maintenance and for the production of milk and growth when the rations are deficient in protein. Ammonium salts and asparagine are more effective than vegetable extracts, but in all cases the non-proteins are much inferior to protein in nutritive value. Armsby's article sets out the many difficulties in the investigation of these intricate questions very clearly.

A. D. Hall.

MINERALOGICAL CHEMISTRY.

The year 1911 has been remarkable for the gaps it has left in the ranks of the workers in Mineralogical Chemistry. The death of J. H. van't Hoff in March last will be felt as an irreparable loss to this as to other branches of science. The brilliant researches on salt deposits, which he happily lived long enough to complete, will stand as one of many enduring monuments of his genius. An appreciation of his work in this field, from the pen of H. E. Boeke, has recently been published.[1] Notable figures have also passed away in A. Michel Lévy and M. H. N. Story-Maskelyne, the latter the doyen of our science; a bibliography of his writings and a short memoir have appeared in the *Mineralogical Magazine*.[2] Among other workers we have to deplore the loss of E. Hussak, N. V. Ussing, and G. Spezia.

The work that has been accomplished during the year, although large in volume, makes little call for special comment. The new minerals described have not been numerous. The most interesting, perhaps, are fermorite, an analogue of apatite containing arsenic; hinsdalite, a sulphato-phosphate of aluminium and lead; and thortveitite, a silicate of scandium. Of the researches which have thrown light on the composition or constitution of known species, those relating to the clintonite group, to nepheline, schwartzembergite, tilasite, parisite, and pearceite are among the most important. Considerable activity continues to be displayed in the study of the physical-chemical problems which have bearings on mineralogy. Some of these will be noted below; we will only here call attention to the work on the ternary systems CaO–Al_2O_3–SiO_2 and AgCl–AgBr–AgI.

Two important new publications have appeared during the year. In the first place, we have to welcome Vol. I of a periodical entitled "Fortschritte der Mineralogie, Kristallographie und Petrographie," published by the newly-formed German Mineralogical Society. In it will be found excellent summaries of recent progress in crystallography and mineralogy. The article on the application of the

[1] *Fortschritte der Mineralogie, Kristallographie und Petrographie*, 1911, **1**, 285.
[2] *Min. Mag.*, 1911, **16**, 149.

phase rule to mineralogical problems, and the review of advances made in our knowledge of meteorites since 1900, will be found worthy of special attention. The notes on new minerals described since 1898 lose much of their value in the absence of any reference to the original sources. The second publication is an ambitious work entitled "Handbuch der Mineralchemie," edited by C. Doelter, assisted by a number of contributors. It seeks to give a complete survey, not merely of our knowledge of the composition of minerals, but also of the best methods of analysis and other cognate topics. The plan of the work is excellent, but to judge by the four parts which have so far appeared, and which are devoted mainly to the treatment of the carbonates, its usefulness is likely to be much impaired by careless editing. Misprints, mis-spellings of proper names, and false references are irritatingly frequent, and tend to shake the confidence of the reader in the general accuracy of the work. We may now proceed to the detailed treatment of our subject, following in the main the order adopted in past years.

General and Physical Chemistry of Minerals.

Silicate Fusions.—In the first place, we must notice that the temperature determinations made up to the present by Day and his colleagues at the Geophysical Laboratory in Washington have been recalculated in terms of the nitrogen thermometer, and a table of corrected values has been drawn up.[3] The melting points of diopside, anorthite, and labradorite are now given as 1391°, 1550°, and 1477° respectively. Albite melts below 1200°, and the change from α-quartz to β-quartz takes place at 575°. A ternary system, lime–alumina–silica, has also been studied in this laboratory.[4] It has already been shown that both the meta- and ortho-silicates of calcium can be obtained from the lime-silica fusion, but no indications of the existence of tricalcium silicate were observed. It has now been discovered that this compound is readily produced when alumina is added to the lime-silica mixture of the proper composition. This substance, which has been isolated in the nearly pure state, appears to be unstable at its melting point. It does not form either eutectics or solid solutions with calcium orthosilicate or with lime. A new, and probably unstable, form of calcium orthosilicate has been discovered; and it has been shown that ferric oxide dissociates at about 1400° with formation of Fe_3O_4, and does not form solid solutions with lime, tricalcium silicate, calcium orthosilicate, or with $3CaO,Al_2O_3$. These researches have an important

[3] A. L. Day and R. B. Sosman, *Amer. J. Sci.*, 1911, [iv], **31**, 341; *A.*, ii, 496.

[4] E. S. Shepherd, G. A. Rankin, and F. E. Wright, *J. Ind. Eng. Chem.*, 1911, **3**, 211; *A*, ii, 725.

bearing on the Portland cement industry. Several other workers have also been active in this field; thus E. Dittler[5] has discussed the difficulties met with in finding the heating and cooling curves of silicates, and using Doelter's methods, has performed illustrative experiments on diopside and on certain felspars, both natural and artificial. He points out that, owing to the small velocity of fusion, the absorption of heat at the melting point is not the chief factor in determining the shape of the heating curve. The values he adopts for the temperatures at which the crystallisation of anorthite and labradorite begins are some 250° lower than the melting points given above. Another interesting research, which we owe to the same author,[6] had for its object the study of the influence of the addition to orthoclase of small quantities of its lithium, rubidium, and cæsium analogues. It was found that cæsium had the greatest effect in increasing the stability of the orthoclase and in promoting its crystallisation, which appears to take place at comparatively low temperatures, 750—800°. If larger quantities of the rubidium or cæsium compounds were employed, the mass ceased to be homogeneous, and different kinds of crystals separated. From this it may be inferred that miscibility can only take place within quite narrow limits. Mixtures of orthoclase and celsian and of orthoclase with andesine were also examined.

Some experiments with mixtures containing orthoclase have also been carried out by C. Neubauer,[7] who finds that in the case of mixtures of artificial leucite, orthoclase, and diopside, melting begins about the fusion point of orthoclase, and ends at a temperature about the mean of all three melting points. On studying the crystallisation phenomena, he finds that the freezing points are lower than the melting points of any of the constituents, and that leucite crystallises out first, followed by diopside. Crystals of orthoclase are not formed.

These, however, are not the only silicates which have been studied from this point of view. H. S. van Klooster,[8] in the course of an examination of a number of binary mixtures, has studied the system Li_2O–SiO_2. He finds that both ortho- and meta-silicates of lithium are formed, and that the two compounds are but slightly miscible. The melting point of the former he gives as 1243°, that of the latter as 1188°. These values are very close to the figures, 1215° and 1180°, given by Rieke and Endell,[9] who have studied

[5] *Zeitsch. anorg. Chem.*, 1911, **69**, 273; *A.*, ii, 96.
[6] *Tsch. Min. Mitt.*, 1911, **30**, 118.
[7] *Föld. Közlöny*, 1911, **41**, 197.
[8] *Zeitsch. anorg. Chem.*, 1910, **69**, 135; *A.*, ii, 111.
[9] R. Rieke and K. Endell, *Sprechsaal*, 1910, **43**, 683; **44**, 97; *A.*, ii, 490, 982.

the same problem. Yet a third value has been obtained for the melting point of lithium metasilicate by F. M. Jaeger,[10] who makes it 1201·8°, that of the corresponding sodium salt being 1088°.

The existence of lead metasilicate as a stable compound has been deduced by P. Weiller [11] from a study of the lead oxide–silica system. He failed to find evidence for the existence of the orthosilicate, and his results are not altogether in harmony with those previously obtained by Hilpert and Nacken.[12] The conditions of formation of the silicates of manganese have been examined in the same way.[13] Manganosite, MnO, was observed among the crystalline products, as well as tephroite, Mn_2SiO_4, and rhodonite, $MnSiO_3$. The eutectic between the two latter lies at 1190°. The mutual relations between the components of binary mixtures of silicates of different metals have also been subjected to thermal analysis. It has been shown, for instance, that $MgSiO_3$ (m. p. 1535°) and $MnSiO_3$ (m. p. 1210°) form a series of solid solutions, with a break at 1328° and 50 molecules per cent. of $MgSiO_3$. Crystals rich in magnesium show the properties of enstatite, those rich in manganese resemble rhodonite. Calcium metasilicate, $CaSiO_3$ (m. p. 1512°), forms a continuous isomorphous series of mixed crystals with the metasilicate of barium, $BaSiO_3$ (m. p. 1438°). The freezing-point curve has a minimum at about 35 molecules per cent. of $BaSiO_3$ and 1000°. Mixtures of the silicates of barium and manganese and of calcium metasilicate with calcium sulphide have also been investigated.[14]

In this connexion it may be noted that R. B. Sosman [15] has studied the published analyses of pyroxenes and pyroxenite rocks, and has plotted the results on a diagram representing a three-component system composed of $MgSiO_3$, $CaSiO_3$, and $FeSiO_3$. He finds that the rock analyses lie in a limited "eutectic field," with the rhombic pyroxenes on one side and the monoclinic pyroxenes on the other, and he considers that the relations observed are in harmony with the experimental data of Allen and White.

Salt Fusions—It is not, however, among the silicates only that the study of cooling curves has led to results of mineralogical importance, for a number of other binary systems have been examined, some of which demand attention here. Italian workers [16] have been particularly busy in this field, and to them we owe our

[10] *J. Washington Acad. Sci.*, 1911, **1**, 49 ; *A.*, ii, 981.
[11] *Chem. Zeit.*, 1911, **35**, 1063 ; *A.*, ii, 983.
[12] See *Ann. Report*, 1910, 227.
[13] F. Doerinckel, *Metallurgie*, 1911, **8**, 201 ; *A.*, ii, 608.
[14] P. Lebedeff, *Zeitsch. anorg. Chem.*, 1911, **70**, 301 ; *A.*, ii, 604.
[15] *J. Washington Acad. Sci.*, 1911, **1**, 54 ; *A.*, ii, 992.
[16] See papers by Sandonnini and others in *Atti R. Accad. Lincei*, 1911, [v]. 20.

knowledge of the behaviour of mixtures of a number of chlorides of univalent and bivalent metals. Some of the bivalent chlorides have also been examined by O. Menge,[17] whilst W. Botta [18] has made a study of the system NaCl–AgCl. He finds that the solidification points of mixtures of silver chloride and salt vary continuously between that of the pure silver compound melting at 460° and that of salt melting at 792°. The crystalline masses which result appear to be homogeneous. The mineral huantajayite, containing 11 per cent. of silver chloride, may be regarded as a member of this series.

These results have been confirmed by C. Sandonnini,[19] who has also found that if lithium chloride is substituted for salt, two kinds of crystals are obtained.

In the hope of throwing some light on the nature of the mixed silver halides which occur as minerals, F. Matthes [20] has made a very complete study of the complex relations of the ternary system AgCl–AgBr–AgI. His results lend no support to the view that iodobromite, 2AgCl,2AgBr,AgI, exists as an independent species, for no compound of all three components could be got from the melt. Two kinds of mixed crystals were, however, obtained. The first form a continuous series, and consist almost entirely of silver chloride and silver bromide, with quite inconsiderable quantities of silver iodide. The second are ternary mixed crystals, and contain silver iodide as an essential constituent. Pure silver iodide was not observed as a product in any of the melts. The compositions of the iodembolites analysed by Prior and Spencer are not in harmony with the results of these experiments, and it is suggested that their crystals were not perfectly homogeneous, but may have consisted of a core rich in silver chloride and bromide, surrounded by a shell containing more silver iodide and bromide. The ternary system formed by the three halides of lead has also been studied by the same author.

The conditions under which mixed crystals of sodium and potassium sulphates are formed, both from fusions and from aqueous solutions, have been examined by R. Nacken.[21] He has found that when fused mixtures are cooled, hexagonal modifications of the salts separate first, which form a complete series of mixed crystals. As the temperature falls, these crystals undergo change, but the production of hexagonal mixed crystals identical with those resulting from aqueous solution at low temperatures is confined to certain

[17] *Zeitsch. anorg. Chem.*, 1911, **72**, 162 ; *A.*, ii, 982.
[18] *Centr. Min.*, 1911, 138 ; *A.*, ii, 293.
[19] *Atti R. Accad. Lincei*, 1911, [v], **20**, i, 758.
[20] *Jahrb. Min. Beil. Band*, 1911, **31**, 342 ; *A.*, ii, 476.
[21] *Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 1016 ; *A.*, ii, 109.

concentrations, the limits being glaserite, $Na_2SO_4,3K_2SO_4$, on the one side, and 49 per cent. of potassium sulphate on the other. From aqueous solutions containing excess of potassium sulphate, glaserite and potassium sulphate separate, but when excess of sodium sulphate is present, mixed crystals composed of glaserite with sodium sulphate occur, together with the latter salt.

Growth and Solution of Crystals.—It has long been known that the presence of impurities in the solution of a crystallisable substance will influence the habit of the crystals which separate. A notable instance of this is found in the behaviour of salt, which is obtained in cubes from pure aqueous solution, but appears in octahedra from solutions to which carbamide has been added. Some light has lately been thrown on this curious phenomenon by the determination of the rates of solution of salt on natural and artificial faces when exposed to the action of unsaturated salt solutions of various strengths.[22] The rate of solution was found to vary with the degree of under-saturation. Moreover, when water containing salt only was used, material was removed slightly faster from the octahedron faces than from those of the cube, but when carbamide was added to the solution, this relation was reversed.

Observations on growth and solution have also been made on other substances; thus, in the case of gypsum,[23] the velocity of solution varies considerably on different faces, the relative values for the three common forms, {010}, {110}, and {111}, being 1 : 1·76 : 1·88 respectively.

In the case of the alums,[24] the habit may be considerably influenced by adding hydrochloric acid to the solution. If a little is added, the forms {211} and {201} appear; further addition of hydrochloric acid causes {201} to increase. The behaviour of meconic acid[25] and of artificial crystals of barytes[26] has also been studied from the same point of view, and it has been shown that the power possessed by some salts of taking up organic dyestuffs is an absorption phenomenon.[27]

Transformation of Polymorphous Substances.—Somewhat discordant statements are current as to the heat-change which accompanies the transformation of aragonite into calcite, and as to the temperature at which the change takes place. It would now appear that the temperature of transformation lies between 465° and 470°, a sudden change in the density of aragonite occurring

[22] A. Ritzel, *Zeitsch. Kryst. Min.*, 1911, **49**, 152; *A.*, ii, 488.
[23] S. Tołłoczko, *Bull. Acad. Sci. Cracow*, 1910, 209; *A.*, ii, 24.
[24] Z. Weyberg, *Chem. Zentr.*, 1910, ii, 1026; *A.*, ii, 263.
[25] P. Gaubert, *Compt. rend.*, 1910, **151**, 1134; *A.*, ii, 101.
[26] H. Gerhart, *Tsch. Min. Mitt.*, 1910, **29**, 185; *A.*, ii, 262.
[27] R. Marc, *Zeitsch. physikal. Chem.*, 1911, **75**, 710; *A.*, ii, 193.

about this point.[28] Measurement of the amounts of heat given out on cooling calcite and aragonite which had been heated to various temperatures led to the conclusion that +2·72 cals. per gram-molecule represents the heat-effect of the change. This number agrees with that obtained by Favre and Silbermann. The results of thermal analysis have established the existence of two kinds of quartz, termed α-quartz and β-quartz respectively, the reversible transformation from one form into the other taking place at 575°. The indices of refraction of quartz have lately been determined at various temperatures, ranging from −140° to +765°, and the existence of these varieties is confirmed by the discovery of a well-marked break at 570°.[29] In the case of leucite, a substance which is birefringent at the ordinary temperature, but becomes isotropic at 714°, the refractive index curve alters its direction; it shows, however, no sudden discontinuity, the change taking place over a considerable temperature interval.

Water of Crystallisation.—A few years ago F. Zambonini [30] contributed to the pages of an Italian periodical a very voluminous discussion of the part played by water in minerals. He has lately published in German a full abstract of this work.[31] His contention is that we must distinguish between water of constitution or crystallisation on the one hand, and dissolved or absorbed water on the other. He maintains that it is possible to make this distinction with certainty by studying the course of dehydration. As the result of numerous experiments, he concludes that many minerals, formerly believed to contain water of constitution, really contain absorbed water, and that many substances, such, for example, as prehnite and apophyllite, contain variable quantities of dissolved water in addition to water of constitution.

Some very interesting observations on the passage of water through certain crystals containing water of crystallisation have been made by H. B. Baker and G. H. J. Adlam [32] during the course of an investigation into the constancy of composition of such substances. Phosphoric oxide was placed in small flasks, which were then closed by crystal plates sealed into their mouths with paraffin. Flasks closed with plates of anhydrous crystals, such as anhydrite, $CaSO_4$, potassium chlorate, or telluric acid, showed no change in weight after exposure to a moist atmosphere for some weeks. On the other hand, flasks closed by plates of gypsum, or of hydrated copper sulphate, barium chloride, and potassium ferrocyanide

[28] P. N. Laschtschenko, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 793 ; *A.*, ii, 886.
[29] F. Rinne and R. Kolb, *Jahrb. Min.*, 1910, ii, 138 ; *A.*, ii, 209.
[30] *Atti R. Accad. Sci. Fis. Mat. Napoli*, 1908, **16**, 1—127.
[31] *Zeitsch. Kryst. Min.*, 1911, **49**, 73.
[32] *Trans.*, 1911, **99**, 507.

showed very perceptible increases, proving that in these cases water had been transmitted by the crystal.

Pressure and Chemical Change.—Van Hise has suggested that under the influence of very high pressures, silicates may be formed from silica and carbonates, water may be squeezed out of hydrated minerals, and combined oxygen may be removed in the same way. G. Spezia[33] has attempted to confirm these views experimentally, but without success. Thus calcium carbonate and hydrated silica did not react when subjected to a pressure of 6000 atmospheres for a year. Limonite, alabaster, and alum, exposed to a pressure of 8000 atmospheres for eight months at 15—24°, were not dehydrated, nor were crystals of göthite affected by keeping them for twenty-six days under a pressure of 9500 atmospheres. Calcite and aragonite remained unchanged after exposure to a pressure of 7000 atmospheres for six months.

Chemical Crystallography.

The two most important investigations undertaken in this field during 1911 are the study of the isomorphism of indium and thallium made by R. C. Wallace[34] and the elaborate examination of derivatives of the quaternary ammonium bases which we owe to A. Ries.[35] The salts of the type $K_3TlCl_6,2H_2O$, of which five were examined, crystallise in the holohedral class of the tetragonal system. Those of the type Rb_2TlCl_5,H_2O are orthorhombic and isomorphous with the potassium and ammonium salts of the same type containing iron. $KTlBr_4,2H_2O$, $(NH_4)_2TlBr_4,2H_2O$, $RbTlBr_4,H_2O$, and $CsTlBr_4$ are all cubic. So far as habit is concerned, the alkalis stand in the order: ammonium, rubidium, cæsium. Chlorine and bromine salts are very similar. On the other hand, the substitution of iron or indium for thallium produces marked changes. The angles vary in a slightly different order, ammonium salts lying between those of rubidium and cæsium, but nearer to the former. The substitution of cæsium for rubidium, or of bromine for iodine, produces about equal effects. Larger effects are observed when indium or thallium is substituted for iron, the changes being roughly proportional to the alteration in the atomic weights. As regards molecular volumes and topic axes, the alkalis form the series K, NH_4, Rb, Cs, ammonium and rubidium being close together. Substitution affects chiefly the χ and ψ values. Substitution in the iron, indium, thallium group has little influence, but indium is more closely related to thallium than to iron.

[33] *Atti R. Accad. Sci. Torino*, 1911, **46**, 682; *A.*, ii, 903.
[34] *Zeitsch. Kryst. Min.*, 1911, **49**, 417; *A.*, ii, 890.
[35] *Ibid.*, 513.

It is impossible to do justice to the very comprehensive work of Ries in the short space at our disposal. Suffice it to say that it consists of a discussion of the chloro- and bromo-platinates and stannates of a very large number of substituted ammonias, several of which have been especially prepared for the purposes of this investigation. The relations exhibited by these substances are very complex, for, although the crystals at first sight apparently exhibit only simple forms of the cubic system, it is found on further investigation that a number of polymorphous forms exist which are often either pseudo-cubic or belong to different sub-classes of the cubic system.

The researches of Tutton have shown that in the series comprising the sulphates and selenates of the alkali metals and the double sulphates and selenates of the type $M_2'SO_4,M''SO_4,6H_2O$, the crystallographic properties of the rubidium salts are intermediate between those of the potassium and cæsium compounds, and that those containing ammonium find a place between the rubidium and cæsium salts. F. M. Jaeger[36] maintains that this regularity is not universal and does not hold in other groups, the morphotropic relations of the alkali metals being in reality very complicated. As an illustration of this he quotes the salts of trichloroacetic acid of the type $CCl_3{\cdot}CO_2K$,$CCl_3{\cdot}CO_2H$, which form an isopolymorphous, in all probability isotetramorphous, series with three monoclinic and one trapezohedral tetragonal modifications. The potassium and ammonium salts are tetragonal, the rubidium salt exhibits one of the monoclinic forms, the cæsium compound the two others, the commoner of the two being pronouncedly pseudo-tetragonal. The thallium salt is tetragonal.

Among minor investigations we may notice the following. H. Baumhauer[37] has continued his examination of the optical and crystallographic character of the platinum double cyanides, and has also studied the picrates of potassium and ammonium. L. Wagner[38] has measured the formates of calcium and strontium; the former salt is rhombic bipyramidal, the latter rhombic bisphenoidal. Attempts to make mixed crystals gave results which led him to conclude that these salts are isotrimorphous. The double chromates of magnesium with cæsium and rubidium have been prepared by T. V. Barker,[39] who finds that they are isomorphous with the corresponding sulphates, and the polymorphism of the phthalylhydrazides, prepared by F. D. Chattaway and D. F. S. Wünsch, has been studied by the same author.[40]

[36] *Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 356.
[37] *Zeitsch. Kryst. Min.*, 1911, **49**, 113; *A.*, i, 431.
[38] *Ibid.*, **50**, 47.
[39] *Trans.*, 1911, **99**, 1326.
[40] *Ibid.*, 2253.

The crystals of some fluorides, silicides, carbides, and borides, prepared by Moissan and his pupils, have been measured by A. de Schulten.[41]

Artificial Formation of Minerals.

A number of minerals have been obtained in minute crystals by heating silica, alumina, lime, potash, or soda with water in a steel tube for twelve to sixteen hours at 350° or 450°.[42] The products, which were identified microscopically, include quartz, orthoclase, albite, oligoclase, analcite, stilbite, andalusite, pyrophyllite, and muscovite, the occurrence of the three latter being especially worthy of note. Isomorphous mixtures of the carbonates of calcium, magnesium, and iron have been prepared by mixing solutions of calcium chloride, magnesium chloride, magnesium sulphate, ammonium sesquicarbonate, and ferrous ammonium sulphate.[43] Gelatinous precipitates are formed, which after a time crystallise. From analyses of the products, it would seem that under these conditions iron and calcium mix in all proportions, but that only small quantities of magnesium are taken up. This is in harmony with the observation that when a magnesium-calcium carbonate is placed in ferrous sulphate, the magnesium is replaced by iron more quickly than the calcium.

Artificial crystals of barytes of some size have been obtained by crystallisation from fused barium chloride and sodium sulphate.[44] A somewhat similar process has resulted in the preparation of a number of artificial apatites, a tribasic arsenate or phosphate being fused with the chlorides of calcium, strontium, barium, or cadmium, or with cadmium bromide. On measuring the hexagonal crystals, it was found that the value of c diminishes when either the metal or the halogen is replaced by another of higher atomic weight, and that a similar change takes place when arsenic is substituted for phosphorus.[45]

The chlorine analogue of spodiosite, $Ca_3(PO_4)_2,CaF_2$, can also be obtained in a similar way,[46] but apparently requires a lower temperature for its production, as on heating to redness, apatite was obtained. This observation explains the rare occurrence of spodiosite in nature.

[41] *Compt. rend.*, 1911, **152**, 1107, 1261; *A.*, ii, 486, 605.

[42] E. Bauer and F. Becke, *Zeitsch. anorg. Chem.*, 1911, **72**, 119; *A.*, ii, 991.

[43] W. Diesel, *Zeitsch. Kryst. Min.*, 1911, **49**, 250; *A.*, ii, 725.

[44] H. C. Cooper, T. S. Fuller, and A. A. Klein, *J. Amer. Chem. Soc.*, 1911, **33**, 845; *A.*, ii, 726.

[45] A. de Schulten, *Compt. rend.*, 1911, **152**, 1404; *A.*, ii, 615.

[46] F. K. Cameron and W. J. McCaughey, *J. Physical Chem.*, 1911, **15**, 463; *A.*, ii, 734.

The formation in nature of smithsonite, $ZnCO_3$, has been imitated by G. Piolti.[47] He suspended a rhombohedron of calcite in a solution of zinc sulphate, and after the lapse of seventeen and a-half years found it coated with mamillary zinc carbonate and with crystals of gypsum. A solution of potassium nitrate left in contact with zinc blende was found to contain sulphate, and fragments of galena similarly treated were found to be coated with crystals of anglesite, $PbSO_4$, nitrite being detected in the solution.

New Minerals.

Achlusite.—This substance is an alteration product of topaz from the Shepherd and Murphy Mine, Tasmania, where it occurs associated with fluorite, cassiterite, wolframite, and topaz.[48] In appearance it resembles steatite.

Bababudanite.—This somewhat uncouth name has been proposed for a soda-amphibole, allied to riebeckite, which occurs in black, radiating, prismatic aggregates associated with cummingtonite in the quartz-magnetite-schist of the Bababudan Hills, Mysore.[49] The cleavage angle is 56°, and the extinction angle somewhat greater than that of riebeckite, from which it differs also in pleochroism. Analysis leads to the formula $2NaFe'''(SiO_3)_2,Fe''Mg_3(SiO_3)_4$.

Batchelorite.—This has been described as a new species in a recently published list of the minerals of Tasmania.[50] It is a hydrated silicate of aluminium, apple-green to greenish-grey in colour, and occurs massive at the Mt. Lyell Mine, Tasmania. The composition is as follows:

SiO_2.	Al_2O_3.	H_2O.	Total.	Sp. gr.
49·4	45·1	5·6	100·1	3·3

Beaverite.—This mineral occurs as very minute, hexagonal plates, forming a canary-yellow, earthy-looking mass at the Horn Silver Mine, near Frisco, Beaver Co., Utah, where it is found with other secondary minerals in the upper part of the deposit.[51] On analysis, its composition was found to agree well with the formula $4CuO,4PbO,3Fe_2O_3,Al_2O_3,8SO_3,16H_2O$, which reduces to

$$CuO,PbO,Fe_2O_3,2SO_3,4H_2O,$$

if the aluminium is regarded as replacing a portion of the iron.

Eichbergite.—A single specimen of an iron-grey, massive mineral has been found embedded in magnesite at Eichberg, on the

[47] *Atti R. Accad. Sci. Torino*, 1911, **46**, 783; *A.*, ii, 902.
[48] W. F. Petterd, *Proc. Roy. Soc. Tasmania for* 1910, 191.
[49] W. F. Smeeth, *Records Mysore Geol. Dept.*, **9**, 85—94; *A.*, ii, 737.
[50] W. F. Petterd, *Proc. Roy. Soc. Tasmania for* 1910, 22.
[51] B. S. Butler and W. T. Schaller, *Amer. J. Sci.*, 1911, [iv], **32**, 418.

Semmering Pass.[52] The results of an analysis, made on half a gram of selected material, agree with the formula:

$$(Cu,Fe)_2S,3(Bi,Sb)_2S_3.$$

The specific gravity is 5·36.

Epinatrolite.—As the result of a study of the natrolite from a quarry in the neighbourhood of Schömitz, near Carlsbad, Thugutt[53] has come to the conclusion that two metameric varieties of this mineral exist. In both the crystal form, the optical properties, and the chemical composition are the same, but, on heating, one is more stable than the other. This is shown by igniting the finely powdered mineral for a few seconds, and then adding solutions of methylene-blue or of silver nitrate followed by potassium chromate. The colour effects produced get weaker the longer the heating was continued. The less stable variety, for which the name epinatrolite is proposed, is common in phonolites, and is believed to be a decomposition product of a member of the sodalite group. The more stable variety is believed to be derived from nepheline.

Fermorite.—This interesting mineral occurs as veins of pale pinkish-white or white material in the manganese ore of Sitapar, Central Provinces, India.[54] The optical characters and the presence on one specimen of a prism of 60° indicate hexagonal symmetry, a conclusion supported by the chemical composition, which conforms to the apatite type, and may be represented by the formula $3[(Ca,Sr)_3(P,As)_2O_8],Ca(OH,F)_2$. The mineral has been named after L. L. Fermor, to whose elaborate investigations of the Indian manganese deposits we owe our knowledge of juddite, sitaparite, hollandite, etc.

Ferriferous Carborundum.—A metallic-looking substance, D 6·7, from the pulsator residues at the Du Toits Pan Diamond Mine, Kimberley,[55] was found on analysis to agree approximately with the formula $Fe_{13}Si_7C_7$. It has not been found in situ, and is probably not an original constituent of the "blue ground," but an artificial product.

Ferritungstite is an alteration product of wolframite, found at the Germania tungsten mine in the Deer Trail mining district of Washington.[56] In appearance it is a pale yellow or brownish-yellow ochre, which, under the microscope, is seen to consist of minute, hexagonal plates. The analytical results lead to the formula $Fe_2O_3,WO_3,6H_2O$.

[52] O. Grosspietsch, *Centr. Min.*, 1911, 433; *A.*, ii, 807.
[53] St. J. Thugutt, *ibid.*, 405; *A.*, ii, 736.
[54] G. F. Herbert Smith and G. T. Prior, *Min. Mag.*, 1911, **16**, 84; *A.*, ii, 1103.
[55] J. R. Sutton, *Nature*, 1911, **87**, 314.
[56] W. T. Schaller, *Amer. J. Sci.*, 1911, [iv], **32**, 161; *A.*, ii, 903.

Gajite.—This mineral closely resembles magnesite in appearance, is apparently homogeneous, and, to judge from its cleavage and optical characters, belongs to the group of rhombohedral carbonates.[57] It occurs in limestone near Plešce, district of Gorski kotar, in Croatia. It dissolves readily in acids, and has the composition:

CaO.	MgO.	CO_2.	H_2O.	Total.	Sp. gr.
37·08	23·85	32·34	6·67	99·94	2·619

Hexahydrite.—A course columnar or fibrous mineral occurs in seams or patches in an altered schistose rock in the district of Lilloet, British Columbia. It is readily soluble in water, and on analysis was found to have a composition agreeing very closely with the formula $MgSO_4,6H_2O$.[58] The specific gravity (1·757) is somewhat greater than that (1·734) recorded for the monoclinic crystals of the artificial salt of the same composition.

Hinsdalite.—An interesting mineral, found at the Golden Fleece mine, near Lake City, Hinsdale Co., Colorado.[59] It has the composition $2PbO,3Al_2O_3,2SO_3,P_2O_5,6H_2O$, and is therefore closely related to svanbergite, the corresponding strontium compound, which appears to occur with it in isomorphous mixture, and to corkite, in which ferric oxide plays the part of alumina. Like these minerals, it belongs to the rhombohedral system, the crystals being rhombohedra approaching cubes in shape, $rr' = 91°18'$, and having a basal cleavage. Viewed in polarised light, the crystals are seen to exhibit anomalies, a positive uniaxial centre being surrounded by biaxial sectors. The refractive indices are $\alpha = 1·670$. $\beta = 1·671$, $\gamma = 1·689$. Sp. gr. = 3·65.

Lublinite.—A name given to a variety of calcite found in felt-like masses in crevices in chalk-marl at Wysokie, Govt. Lublin, Russian Poland.[60]

Molengraaffite.—Small, yellowish-brown prisms, probably of monoclinic symmetry, occur as a constituent of lujaurite, a rock of the nepheline-syenite group, in the Pilandsberg, Transvaal.[61] They exhibit a perfect cleavage parallel to the orthopinacoid, and the refraction and birefringence are high ($\alpha = 1·735$, $\gamma = 1·770$). Their composition, as determined by Pisani, is as follows:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3	FeO.	MnO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
28·90	27·70	3·75	0·95	2·07	2·72	19·00	2·38	10·30	0·60	1·00	99·37

[57] Fr. Tućan, *Centr. Min.*, 1911, 312; *A.*, ii, 498.

[58] A. A. Johnston, *Summary Report Geol. Survey Branch Dep. of Mines, Canada*, 1911, 256.

[59] E. S. Larsen, jun., and W. T. Schaller, *Amer. J. Sci.*, 1911, [iv], **32**, 251; *A.*, ii, 1102.

[60] J. Morozewicz, *Zeitsch. Kryst. Min.*, 1910, **48**, 522; *A.*, ii, 121.

[61] H. A. Brouwer, *Centr. Min.*, 1911, 129; *A.*, ii, 296.

Morganite.—This name has been suggested for the rose-pink beryl from California, which is suitable for use as a gem.[62] It is, however, hard to discover what useful scientific purpose is served by associating the name of an American millionaire with a particular occurrence of a well-known mineral.

Muthmannite.—The tellurides of gold and silver grouped together under the name krennerite differ somewhat widely in composition, and Zambonini[63] proposes to establish a separate species under the name *muthmannite* for those of the type (Ag,Au)Te, containing about 20 per cent. of silver, retaining the name *krennerite* for those of the type $[Au(Ag)]Te_2$, of which the silver content is small. A specimen of the former mineral from Nagyag consisted of imperfect crystals elongated in one direction, parallel to which there was a good cleavage. The crystals were pale brass-yellow in colour, and were found on analysis to contain 26·36 per cent. of silver, and to have the formula (Ag,Au)Te.[64]

Natramblygonite.—The mineral occurs massive in pegmatite near Canon City, Colorado.[65] It resembles amblygonite in appearance, but contains much sodium ($Na_2O = 11·23$ per cent.), and but little lithium ($Li_2O = 3·21$ per cent.). The formula is

$$(Na,Li)Al(OH,F)PO_4,$$

analogous to that of amblygonite.

Neocolemanite.—A mineral forming a considerable deposit, interbedded with black, carbonaceous shales, near Lang, Los Angeles Co., California, has been termed neocolemanite on account of slight divergences in its optical and crystallographic properties from those of colemanite, with which it otherwise appears to be identical.[66] It would seem, however, that these divergences vanish if a slightly different orientation be given to the crystals, the faces 001, 010, and 100 of neocolemanite being taken as 001, 010, and $\bar{2}01$ of colemanite.

Poechite.—A manganese ore of the composition $H_{16}Fe_8Mn_2Si_3O_{29}$ occurs at Vares, in Bosnia. In colour it is red to chesnut-brown, and is believed to represent a new species.[67]

Stewartite.—A name proposed for a variety of bort, apparently containing metallic iron, from the Kimberley diamond mines.[68]

Stitchtite.—Occurs in irregular masses and veins of a rose-pink

[62] G. Kunz, *Amer. J. Sci.*, 1911, [iv], **31**, 81.

[63] F. Zambonini, *Zeitsch. Kryst. Min.*, 1911, **49**, 246; *A.*, ii, 734.

[64] C. Gastaldi, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iiia], **17**, 24; *A.*, ii, 901.

[65] W. T. Schaller, *Amer. J. Sci.*, 1911, [iv], **31**, 48; *A.*, ii, 121.

[66] A. S. Eakle, *Bull. Dep. Geol. Univ. California*, 1911, **6**, 179; *A.*, ii, 901.

[67] F. Katzer, *Chem. Zentr.*, 1911, i, 1650.

[68] J. R. Sutton, *Nature*, 1911, **87**, 550.

to deep purple colour in serpentine at Dundas, Tasmania. Under the microscope it appears to consist of strongly birefringent fibres and tufts sometimes radially disposed about nuclei of chromite. The composition is as follows:

Cr_2O_3.	Fe_2O_3.	MgO.	CO_2.	H_2O.	Total.	Sp. gr.
11·5	9·0	36·0	7·2	36·1	99·8	2·12

The mineral dissolves with effervescence in hydrochloric acid, affording an intensely bright green solution. It was formerly mistaken for kämmererite, a member of the chlorite group.[69]

Thortveitite.—This remarkable mineral was found in pegmatite in Iveland, south Norway, associated with euxenite, monazite, and beryl. It forms rosettes of radial structure, some of the individuals reaching considerable dimensions. The system is orthorhombic, $a:b:c=0{\cdot}7456:1:1{\cdot}4912$. The forms present are 111, 211, and 110, the latter being a plane of cleavage and twinning. The crystals are greyish-green in colour, and translucent to transparent. The plane of the optic axes is 010, the acute negative bisectrix being perpendicular to 001. The mineral exhibits strong refraction ($\alpha=1{\cdot}7625_{\text{green}}$) and birefringence. Its specific gravity is 3·57. Preliminary analyses have led to the interesting conclusion that the composition of the mineral is $R_2'''O_3,2SiO_2$, where R''' stands for scandium and metals of the yttrium group, the former largely preponderating. A direct determination of the scandium gave $Sc_2O_3=37$ per cent. The mineral is therefore a scandium silicate.[70]

Vaterite.—This name has been suggested for an unstable variety of calcium carbonate, which usually occurs as spherulites, although sometimes in optically biaxial needles. It is distinguished from aragonite by its lower specific gravity (2·6 about) and weak birefringence.[71]

Yttrofluorite.—The mineral occurs in pegmatite in north Norway.[72] It is isotropic, and possesses imperfect octahedral cleavage. The physical characters and composition vary slightly in different specimens. One sample of density 3·557 and refractive index 1·4572 (sodium light) gave, on analysis, results agreeing with the formula $20CaF_2,3YF_3$.

In addition to the above, investigations have been published of a few other substances, some of which may prove to be new minerals. Among them we may notice a titano-tantalate of rare earth metals, from the State of Espirito Santo, Brazil,[73] and two hydrated

[69] W. F. Petterd, *Proc. Roy. Soc. Tasmania for* 1910, 167.

[70] J. Schetelig, *Centr. Min.*, 1911, 721; *A.*, 1912, ii, 56.

[71] *Vide* C. Doelter's *Handbuch der Mineralchemie*, I, 113.

[72] T. Vogt, *Centr. Min.*, 1911, 373; *A.*, ii, 733.

[73] J. M. de Padua e Castro, *Revista Chim.*, 1910, **6**, 365; *A.*, ii, 735.

silicates of aluminium allied to allophane from the neighbourhood of Aywaille, Belgium.[74] The first of these latter may be represented as $Al_2O_3,SiO_2,7\frac{1}{2}H_2O$, and is easily attacked by acids; the second has the formula $4Al_2O_3,5SiO_2,15H_2O$, and resists the action of acids.

Mineral Analyses.

Aegirite.—Good, blackish-green crystals approximating closely to the theoretical composition $Na_2Fe_2Si_4O_{12}$ occur in pegmatite in the Quincy granite, Mass., U.S.A.[75] The axial ratios are $a:b:c=1{\cdot}1044:1:0{\cdot}6043$; $\beta=73°27'$. The crystals are pleochroic, and the extinction angle is 6°.

Allophane.—The nature of the hydrated aluminium silicates, *allophane*, *halloysite*, and *montmorillonite*, has often been discussed; and while, on the one hand, the individuality of these species has been maintained, it has been held, on the other, that they are merely loose combinations or mixtures of colloidal silicic acid with colloidal alumina. St. J. Thugutt[76] finds support for the former view in the behaviour of these substances towards organic dyestuffs, but his conclusions have been traversed by H. Stremme.[77]

Alunite Group.—A useful discussion of this group has lately been given by W. T. Schaller.[78] The numerous minerals composing the group are all rhombohedral, and may be represented by the general formula $[R'''(OH)_2]_6R''[M]_2[M_2]$. They may be conveniently divided into three sub-groups, of which alunite, hamlinite, and beudantite may be taken as types. It is suggested that goyazite is identical with hamlinite; and apatelite, raimondite, pastreite, cyprusite, and utahite are all united with carphosiderite, to which the formula $H_2O,3Fe_2O_3,4SO_3,6H_2O$ is assigned.

An analysis of alunite, found in liparite, has been published by U. Panichi.[79]

Atacamite.—H. Ungemach[80] has made an elaborate crystallographic examination of this mineral, and has observed a number of new forms. He adopts the orientation given by Phillips and by Lévy, and finds $a:b:c=0{\cdot}87808:1:1{\cdot}32710$. He regards the *paratacamite* of G. F. Herbert Smith as a complex twin of ordinary atacamite. Analyses of material from Antofagasta and from Boleo gave results agreeing closely with one another and with the formula $CuCl_2,3Cu(OH)_2$.

[74] G. Moressée, *Bull. Soc. géol. Belgique*, 1911, **37**, 270.
[75] C. Palache and C. H. Warren, *Amer. J. Sci.*, 1911, [iv], **31**, 533; *A.*, ii, 614.
[76] *Centr. Min.*, 1911, 97, 276; *A.*, ii, 210, 501.
[77] *Ibid.*, 205; *A.*, ii, 406.
[78] *Amer. J. Sci.*, 1911, [iv], **32**, 359; *A.*, ii, 1101.
[79] *Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 656; *A.*, ii, 210.
[80] *Bull. Soc. franç. Min.*, 1911, **35**, 148; *A.*, ii, 1100.

Bauxite.—An account of the occurrence and employment in commerce of this mineral has been given by A. Gautier.[81] The variations in its composition are illustrated by analyses.

Bertrandite.—The chemical formula, $H_2Be_4Si_2O_9$, of this rare mineral has been confirmed by the analysis of good material from Iveland, South Norway.[82] The crystallographic and optical characters were also determined. The optic axial plane is parallel to 010, and the obtuse bisectrix perpendicular to the base. $2V = 74°41'$, and $\alpha = 1{\cdot}5914$, $\beta = 1{\cdot}6053$, $\gamma = 1{\cdot}6145$ (all for Na light). Sp. gr. = 2·597.

Beryl.—Much attention has been paid of late to the beautiful beryls which occur in the pegmatites of Madagascar, and it would appear that two types can be recognised.[83] One, ordinary aquamarine, of prismatic habit and exhibiting but few faces; the other of tabular habit, and rich in faces. Crystals of the second type contain considerable quantities of alkali metals, particularly of cæsium, and are denser than those of the first type, and have higher indices of refraction. Lacroix,[84] however, has pointed out that so far as composition is concerned, the analyses hitherto published indicate the existence of a continuous series of compounds with corresponding gradations in density and refractivity.

Bismuth Ochre.—Amorphous bismuth ochres occur at Pala, San Diego Co., California. A grey sample was found to consist mainly of bismuth hydroxide. A yellow specimen had the composition of pucherite, $BiVO_4$, whilst another yellow specimen proved to be a mixture of vanadate and hydroxide. These results tend to confirm the view that natural bismite is a hydroxide.[85]

Bismutosphaerite.—Analyses of this rare mineral published by S. D. Kusnetzoff [86] agree fairly well with the formula Bi_2CO_5.

Blende.—The well-known transparent yellow blende from Picos de Europa was found, on spectroscopic examination, to contain indium, gallium, and germanium. Iron was present in very varying proportions in all the specimens examined; one which was nearly colourless contained 0·066 per cent. of ferrous sulphide only. Water extracts traces of the chlorides of calcium, potassium, sodium, and lithium from the finely powdered mineral.[87]

[81] *Rev. gén. Chim. pure appl.*, 1910, **13**, 389; *A.*, ii, 497.
[82] T. Vogt, *Zeitsch. Kryst. Min.*, 1911, **50**, 6.
[83] L. Duparc, M. Wunder, and R. Sabot, *Bull. Soc. franç. Min.*, 1911, **34**, 131, 239; *A.*, ii, 1105.
[84] A. Lacroix and E. Rengade, *ibid.*, 123; *A.*, ii, 736. See also *Ann. Report* for 1910.
[85] W. T. Schaller, *J. Amer. Chem. Soc.*, 1911, **33**, 162; *A.*, ii, 293.
[86] *Bull. Acad. Sci. St. Pétersbourg*, 1911, 897; *A.*, ii, 1104.
[87] R. Llord y Gamboa, *Anal. Fis. Quim.*, 1910, **8**, 413; *A.*, ii, 733.

Blomstrandine.—Black crystals in pegmatite from Miask, supposed to be aeschynite, have proved, on analysis, to be identical with Brögger's blomstrandine, a titano-columbate of yttrium earths.[88]

Blomstrandite.—A massive mineral of greenish-brown colour, found in pegmatite at Ambolotara, Madagascar, was found on analysis to be a uraniferous columbo-titanate similar in composition to the substance from Nohl, Sweden, described by Lindström under the name blomstrandite in 1874.[89] It must not be confused with blomstrandine.

Calaverite.—It is interesting to notice that a study of the freezing-point curve of the system gold–tellurium has shown the presence of a maximum corresponding with the compound $AuTe_2$, melting at 464°. There are also two eutectic points at 416° and 447° respectively, corresponding with 12 and 47 atomic percentages of gold. There is no indication of the formation of solid solutions.[90].

Cancrinite.—A re-examination of the material from Brevig, Norway, analysed by Lemberg in 1887 showed it to be quite fresh and pure except for a trace of ferric oxide, to which it owes its red colour. The formula deduced from the analysis of this material is $H_{18}Ca_5Na_{24}Al_{22}Si_{24}C_6O_{119}$. Other specimens examined proved to be impure, chiefly owing to the presence of secondary natrolite. Cancrinite is analogous in constitution to nepheline and sodalite; on alteration it passes to an end-product consisting mainly of natrolite.[91]

Clintonite Group.—An elaborate investigation of this group is due to E. Manasse,[92] who has analysed with great care three different specimens of *ottrelite* from three localities in the Apuan Alps (analyses I–III below), as well as five other varieties, including masonite (IV), sismondine (V), ottrelite from Ottré in the Ardennes (VI), ottrelite from Mont Fenouillet (VII), and Venasquite (VIII). An equally careful analysis (IX) of a variety called salmite has been made by H. de Rauw.[93] The specimen came from near Ottré, where it occurs in tables of a dark greenish-yellow colour. Its cleavages are better, and its pleochroism less intense, than those of chloritoid, and it contains almost twice as much manganese as the original salmite from Vielsalm:

[88] O. Hauser and H. Herzfeld, *Centr. Min.*, 1910, 756; *A.*, ii, 46.

[89] A. Lacroix, *Bull. Soc. franç. Min.*, 1910, **33**, 321; *A.*, ii, 295.

[90] G. Pellini and E. Quercigh, *Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 445; *A.*, ii, 45.

[91] S. J. Thugutt, *Jahrb. Min.*, 1911, i, 25; *A.*, ii, 298.

[92] *Atti Soc. Toscana Sci. Nat. Memorie*, 1910, **26**, 121, and *ibid.*, *Proc. Verb.* 1911, **20**, 29.

[93] *Ann. Soc. Géol. Belgique*, 1911, **38**, 209 B.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
I.	24·37	37·03	5·36	21·91	0·52	0·16	4·32	7·16	100 83	3·44
II.	26·07	37·01	3·97	24·76	tr.	0·12	1·90	7·03	100·86	3·51
III.	25·36	38·99	2·54	23·06	tr.	0·24	3·16	7·28	100·63	3·56
IV.	24·56	34·57	5·93	27·20	1·14	—	0·36	6·64	100·40	3·54
V.	25·36	42·58	0·72	18·02	0·53	0·18	5·96	7·50	100·85	3·45
VI.	42·93	29·60	0·86	15·43	3·75	—	2·12	5·48	100·17	3·25
VII.	30·02	34·70	4·76	20·54	1·42	1·17	1·71	6·71	101·03	3·60
VIII.	37·87	31·12	3·25	20·48	0·62	tr.	1·44	5·80	100·58	3·40
IX.	25·50	33·57	2·01	9·16	16·63	0·91	4·40	6·96	99·79	—

I–III and VII show traces of TiO_2. IX contains also 0·65 P_2O_5.

The ratios deduced from the first five analyses lead accurately to the formula $H_2FeAl_2SiO_7$. A similar result is obtained if it be assumed that the excess of silica shown in analyses VI–VIII is due to admixed quartz, an assumption amply justified by microscopical examination. In the case of salmite (IX), after deducting from the silica 2·12 per cent. present as quartz, the ratios are:

$$SiO_2 : Al_2O_3 : FeO : H_2O = 1 : 0{\cdot}8775 : 1{\cdot}25 : 0{\cdot}9875.$$

This divergence from the type is possibly due to part of the manganese being present as Mn_2O_3.

Corundum.—The colour of the oriental sapphire has been imitated in the artificial product by adding small quantities of ferric and titanic oxides to the alumina used. It has now been shown that small quantities of titanium (0·03—0·058 per cent. of TiO_2) are also present in natural sapphires, and it is therefore concluded that the colour of the gem is due to titanium present as an oxide or as a titanate of iron.[94]

Cuprodescloizite.—A specimen from the Old Yuma mine, Arizona, contained 11·64 per cent. CuO, and agreed with the ordinary formula $R_3(VO_4)_2,R(OH)_2$, which also expresses the composition of small, black crystals of *descloizite* from Argentina.[95]

Dolomite.—A crystalline, ferriferous dolomite of the formula $3CaCO_3,2MgCO_3,FeCO_3$ has been found in the Simplon Tunnel.[96]

Eglestonite.—The oxychloride of mercury, Hg_4Cl_2O, found originally at Terlingua, Texas, also occurs in minute cubic crystals in a siliceous matrix in serpentine in San Mateo Co., California. An analysis made on 0·025 gram was in agreement with the accepted formula.[97]

Emplectite.—A specimen of this mineral was found to have the formula $CuBiS_2$.[98]

Euxenite.—Crystal fragments from the pegmatite of Sätersdal,

[94] A. Verneuil, *Compt. rend.*, 1910, **151**, 1063; *A.*, ii, 43.
[95] F. N. Guild, *Zeitsch. Kryst. Min.*, 1911, **49**, 321; *A.*, ii, 902.
[96] G. Lincio, *Atti R. Accad. Sci. Torino*, 1911, **46**, 969; *A.*, ii, 1101.
[97] A. F. Rogers, *Amer. J. Sci.*, 1911, [iv], **32**, 48; *A.*, ii, 807.
[98] E. Priwoznik, *Österr. Zeitsch. Berg. Hüttenwesen*, 1910, **58**, 713; *A.*, ii, 991.

south Norway, have been carefully examined by H. Lange.[99] His results are very similar to those obtained by Rammelsberg for *polycrase* from Hitterö, and support Broegger's view that euxenite and polycrase are the end-members of a series, in which the ratio $M_2O_5 : TiO_2$ varies between the limits 1:2 and 1:6. Full details of the analytical methods employed are given in this paper, together with a discussion of the method of separating tantalic, niobic, and titanic acids by means of ammonium salicylate. A specimen of the same mineral from Ambolotara, Madagascar, had a composition closely resembling that of the material from Arendal and from Eydland.[1]

Fayalite.—A complete crystallographic and optical examination of the small, orthorhombic crystals from the Cuddia Mida crater in the island of Pantelleria, has been made by J. Soellner.[2] The composition may be expressed by the formula $Mg_2SiO_4,10Fe_2SiO_4$, portions of the magnesium, iron, and silicon being replaced by calcium, manganese, and titanium respectively. The relations between the optical constants and the percentage of ferrous iron are in harmony with the results of Penfield and Forbes.[3] The axial ratios and refractive indices are as follows:

$$a : b : c = 0{\cdot}4600 : 1 : 0{\cdot}5811;$$

$\alpha = 1{\cdot}8044$, $\beta = 1{\cdot}8383$, $\gamma = 1{\cdot}8462$; $2V = 51°$ (yellow Hg light). The optic axial plane is 001. The acute negative bisectrix is perpendicular to 010.

Felspar Group.—Analyses of two potash-felspars and of eight plagioclases ranging from $Ab_{3{\cdot}5}An$ to $Ab_{5{\cdot}1}An$ have been given by I. Nordenskjöld[4] in the course of a general account of the minerals found in the pegmatite of Ytterby, Sweden. A labradorite of the composition $Ab,An_{2{\cdot}108}$ from Pinacate, Sonora, Mexico, has been examined by Y. S. Bonillas,[5] and may be compared with the mineral described by Ford and Bradley from the Altai Mountains.[6] A microperthite from the Ilmen Mountains and an oligoclase-albite from the south Urals have been described by W. W. Arschinow.[7] The former can be obtained in transparent pieces, which lend themselves to optical examination; it contains barium, and may be represented by the formula $Or_{59}Ab_{40}Ce_1$. The latter is approximately $Ab_{80}An_{20}$.

[99] *Zeitsch. Naturwiss. Halle*, 1910, **82**, 1; *A.*, ii, 499.
[1] A. Lacroix, *Bull. Soc. franç. Min.*, 1910, **33**, 321; *A.*, ii, 295.
[2] *Zeitsch. Kryst. Min.*, 1911, **49**, 138; *A.*, ii, 502.
[3] *A.*, 1896, ii, 373.
[4] *Bull. Geol. Inst. Univ. Upsala*, 1910, **9**, 183; *A.*, ii, 296.
[5] *Parergones Inst. Geol. Mexico*, 1910, **3**, 427.
[6] *Ann. Report*, 1910, 244.
[7] *Publication of the Petrographical Institute, Lithogræa, Moscow*, 1911, 12 pp.

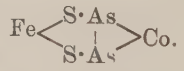
As the result of an examination of a large number of felspars, Barbier found that orthoclases always contain small quantities of lithium and sometimes of rubidium, but that these elements do not occur in microcline.[8] These conclusions have been contested by W. I. Vernadsky and Mlle. E. Revutsky,[9] but in a criticism of their work Barbier maintains his position,[10] and still regards the presence or absence of lithium as constituting a fundamental difference between the species.

Garnet Group.—Analyses have been published of specimens of andradite from Assynt, Sutherlandshire,[11] from Sardinia,[12] and from Berks County, Pennsylvania.[13] The first is a dark brown melanite of rhombic dodecahedral habit, and contains 6·74 per cent. of TiO_2; the second is a honey-yellow garnet, and agrees very closely with the formula $Ca_3Fe_2(SiO_4)_3$, part of the iron being replaced by aluminium; the third is very similar to the second.

Glauberite.—Brick-red nodules from Varangéville, near Nancy, have a composition agreeing with the usual formula,

$$Na_2SO_4,CaSO_4.$$[14]

Glaucodote.—If heated in a vacuum this mineral loses a little sulphur and arsenic; if roasted and again heated, more sulphur and arsenic are obtained, until finally 4·38 per cent. of the sulphur and 23·37 per cent. of the arsenic contained in the mineral are found in the distillate.[15] The effect of roasting is apparently to produce some disulphide, which on heating decomposes into monosulphide and sulphur. These experiments support the view that glaucodote has the formula



Goldschmidtite.—The individuality of this mineral has been disputed by Palache, who on crystallographic grounds regarded it as identical with *sylvanite*. It appears, however, that its composition is approximately represented by the formula $(Au,Ag)_2Te_5$, and it may therefore be properly regarded as a separate species.[16]

Herderite.—A crystallographic examination of the material from Mt. Apatite, Auburn, Maine, has shown that the substance crystal-

[8] *Ann. Report*, 1909, 211.
[9] *Compt. rend.*, 1910, **151**, 1372; *A.*, ii, 122.
[10] *Bull. Soc. franç. Min.*, 1911, **34**, 117; *A.*, ii, 735.
[11] A. Gemmell, *Trans. Edinburgh Geol. Soc.*, 1910, **9**, 417; *A.*, ii, 300.
[12] A. Serra, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1910, [iii], **16**, 222; *A.*, ii, 123.
[13] E. F. Smith, *Proc. Acad. Nat. Sci. Philadelphia*, 1911, **62**, 538; *A.*, ii, 501.
[14] V. Dürrfeld, *Mitt. geol. Landesanstalt Elsass-Lothringen*, 1911, **7**, 345; *A.*, ii, 295.
[15] A. Beutell, *Centr. Min.*, 1911, 411; *A.*, ii, 728.
[16] C. Gastaldi, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iiia], **17**, 22; *A.*, ii, 901.

lises in the monoclinic system, two crystals being commonly twinned together to form a pseudorhombic individual. A partial analysis proved that the substance was a hydrofluorherderite,

$$Ca[G(F,OH)]PO_4,$$

but as the angles approach nearer to those given by Penfield for hydroherderite than to those given by Dana for the hydrofluorherderite from Stoneham, it is considered probable that Penfield's angles hold for all varieties of the mineral.[17]

Howlite.—Nodular masses of this remarkable calcium silico-borate occur at Lang, Los Angeles Co., California.[18] The composition may be represented by the formula $Ca_2B_4O_8,B(OH)_3,H_2SiO_3$.

Hypersthene.—Specimens found in andesite rocks on the borders of Transylvania and Bukovina have been studied by V. C. Butureanu.[19] The crystals, which have the ratios

$$a:b:c=0{\cdot}97:1:0{\cdot}57,$$

are often twinned. The three following analyses I–III were made on black, green, and greenish-grey crystals respectively:

	SiO_2.	Al_2O_3.	Fe(Mn)O.	CaO.	MgO.	H_2O.	Total.
I.	49·43	3·10	14·75	4·17	27·00	1·66	100·11
II.	49·80	1·40	12·00	10·25	26·00	0·84	100 29
III.	50·15	2·02	10·24	8·00	28·85	0·95	100·21

Jamesonite.—W. T. Schaller [20] is of opinion that the best analyses of this mineral are more in harmony with the formula

$$4PbS,FeS,3Sb_2S_3,$$

proposed by Loczka, than with the more complicated formula, $7(Pb\frac{4}{5}, Fe\frac{1}{5})S,4Sb_2S_3$, adopted by Spencer. The mineral *warrenite*, held by Spencer to be identical with *jamesonite*, is shown to be a mixture of *jamesonite* and *zinkenite*, PbS,Sb_2S_3.

Kaolinite.—In the course of a study of the heating curve of this mineral, Mellor and Holdcroft [21] have shown that an endothermic reaction occurs about 500°. This may be interpreted as indicating the decomposition of the kaolinite into silica, alumina, and water. At 800° an exothermic reaction takes place, due to a change in the physical condition of the alumina. They regard kaolinite as an aluminodisilicic acid, $\begin{matrix}(HO)_2\\(HO)_2\end{matrix}\!\!>\!Al_2\!<\!\begin{matrix}O{\cdot}SiO\\O{\cdot}SiO\end{matrix}\!\!>\!O$, and point out that other silicates may be referred to similar acids. The composition of a specimen from Northumberland,[22] occurring in silvery-white

[17] W. E. Ford, *Amer. J. Sci.*, 1911, [iv], **32**, 283; *A.*, ii, 1102.

[18] A. S. Eakle, *Bull. Dept. Geol. Univ. California*, 1911, **6**, 179; *A.*, ii, 901.

[19] *Ann. Sci. Univ. Jassy*, 1910, **6**, 287.

[20] *Zeitsch. Kryst. Min.*, 1911, **48**, 562; *A.*, ii, 209.

[21] J. W. Mellor and A. D. Holdcroft, *Trans. Eng. Ceramic Soc.*, 1911, **10**, 94; *A.*, ii, 607.

[22] R. C. Burton, *Proc. Univ. Durham Phil. Soc.*, 1911, **4**, 24; *A.*, ii, 735.

scales, showing a basal cleavage and a biaxial interference figure, agreed very closely with the formula $Al_2O_3,2SiO_2,2H_2O$.

Marcasite.—The question as to the state of oxidation of the iron in this mineral has often been discussed. Recent experiments, in which the substance has been heated in a sealed tube at 250° with carbon tetrachloride or fused with bismuth chloride in an atmosphere of carbon dioxide, indicate that the iron is all present in the ferrous state.[23]

Mispickel.—An attempt has been made to elucidate the constitution of this mineral by studying its behaviour when heated in a vacuum (compare glaucodote, p. 258 above). In these circumstances small quantities of sulphur and of arsenic sulphide distil over, together with arsenic amounting to 12·2 per cent. of the substance taken. The whole of the arsenic is not expelled, even if the heating be continued for a long time, but both the arsenic and sulphur can readily be driven off if the substance is first roasted and then distilled in a vacuum. The conclusion is drawn that the formula is $Fe_2As_2S_2$, and the constitution analogous to that of glaucodote.[24]

Nepheline.—In the case of natural minerals it is often impossible to deduce satisfactory formulæ from the results of analyses carried out with all care on apparently pure and homogeneous material. The suggestion has therefore been made that in such cases we are dealing with homogeneous mixtures of different compounds, some other constituent being present in solid solution in the mineral.[25] This theory has been applied to explain the divergence of nepheline from the simple formula $NaAlSiO_4$. Carefully selected material from Eikaholmen, Norway, gave the ratios:

$$SiO_2 : Al_2O_3 : Na_2O = 2{\cdot}23 : 1{\cdot}00 : 0{\cdot}98.$$

The analyses published by Morozewicz yielded similar results, the ratio $SiO_2 : Al_2O_3$ varying from 2·11 to 2·21. It is therefore concluded that the excess of silica is present in solid solution.

Another view of the constitution of this substance has been propounded by W. T. Schaller,[26] who regards it as a mixture of the four isomorphous molecules, $NaAlSiO_4$, $KAlSiO_4$, $CaAl_2Si_2O_8$, $NaAlSi_3O_8$, just as the plagioclase felspars are mixtures of the molecules $NaAlSi_3O_8$ (albite), $CaAl_2Si_2O_8$ (anorthite), $NaAlSiO_4$ (carnegieite), and $KAlSi_3O_8$ (microcline).

Olivine Group.—The data correlating optical properties and chemical composition in this group have been brought together by

[23] G. W. Plummer, *J. Amer. Chem. Soc.*, 1911, **33**, 1487; *A.*, ii, 901.
[24] A. Beutell, *Centr. Min.*, 1911, 316; *A.*, ii, 485.
[25] H. W. Foote and W. M. Bradley, *Amer. J. Sci.*, 1911, [iv], **31**, 25; *A.*, ii, 122.
[26] *J. Washington Acad. Sci.*, 1911, **1**, 109; *A.*, ii, 992.

H. Backlund,[27] who has also made numerous determinations of refractive indices and several new analyses. An abstract of this memoir, which appeared originally in Russian, is now available for English readers.

Orthite.—Irregular masses of this mineral found in a felspar quarry at Impilaks, on Lake Ladoga, were found on analysis to contain up to 1 per cent. of scandium oxide.[28] Wiikite, another mineral containing appreciable quantities of scandium, occurs at the same locality.

Parisite.—A considerable addition to our knowledge of this rare fluo-carbonate of cerium, lanthanum, and didymium has been made by the study of the small, yellow crystals of rhombohedral habit found in pegmatite at Quincy, Massachusetts.[29] The refractive indices, $\omega = 1{\cdot}676$ and $\epsilon = 1{\cdot}757$, are considerably higher than those previously accepted. The composition may be expressed by the formula $(R'''F)_2Ca(CO_3)_3$, where $R''' = Ce,La,Di$, and it is suggested that *synchysite* from Greenland is probably a variety of this mineral containing admixed calcite.

Pearceite.—The formula $9(Ag,Cu)_2S,As_2S_3$ was assigned to this mineral by Penfield in 1896, and it was regarded by him as the arsenic analogue of *polybasite*, $9Ag_2S,Sb_2S_3$. The results of a careful analysis[30] of black, platy crystals from the Veta Rica Mine, Coahuila, Mexico, agree, however, very closely with the formula $8(Ag,Cu)_2S,As_2S_3$, and it would appear also that the published analyses of polybasite agree better with a formula of this type than with that which has hitherto been generally accepted.[31]

Two analyses of the latter mineral recently made by H. Ungemach[32] on material from Las Chiapas, Sonora, and from Sonora, Mexico, respectively, are in harmony with this conclusion.

Phosphorite Group.—A study of the published analyses of *collophanite*, *dahllite* (=*podolite*), and *francolite* (=*staffelite*) has led W. T. Schaller to the conclusion that the following formulæ are the most probable[33]:

Dahllite	$9CaO,3P_2O_5,CaO,CO_2,H_2O$
Francolite	$9CaO,3P_2O_5,CaF_2,CO_2,H_2O$
Collophanite	$9CaO,3P_2O_5,CaO,CO_2,H_2O+nH_2O$.

Platinum.—The geological conditions under which this metal

[27] *Trav. Musée Géol. Pierre le grand Acad. Sci. St. Pétersbourg*, 1909, **3**, 77; *A.*, ii, 616.

[28] R. J. Meyer, *Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 379; *A.*, ii, 406.

[29] C. Palache and C. H. Warren, *Amer. J. Sci.*, 1911, [iv], **31**, 533; *A.*, ii, 614.

[30] F. R. van Horn and C. W. Cook, *ibid.*, 518; *A.*, ii, 614.

[31] F. R. van Horn, *ibid.*, **32**, 40; *A.*, ii, 807.

[32] *Bull. Soc. franç. Min.*, 1910, **33**, 375; *A.*, ii, 614.

[33] *J. Washington Acad. Sci.*, 1911, **1**, 151; *A.*, ii, 1102.

occurs in the Urals have been examined by L. Duparc,[34] and fifteen analyses of native platinum collected from stream beds in various localities in that district have been made by H. C. Holtz.[35]

Plumbojarosite.—This rare mineral has been found lately in some abundance at several localities in Beaver County, Utah.[36] It is dark brown in colour, and micaceous in structure. Under the microscope the crystals are seen to be thin, uniaxial, hexagonal plates, optically negative, and strongly birefringent. Analysis gave results agreeing well with those previously obtained and in harmony with the formula $PbO,3Fe_2O_3,4SO_3,6H_2O$.

Powellite.—White plates analysed by S. D. Kusnetzoff[37] gave results agreeing closely with the formula $CaMoO_4$. They thus differ considerably from the Idaho specimens, in which part of the molybdenum is replaced by tungsten.

Pyrites.—An elaborate study of the figures produced by etching polished faces of crystals of iron pyrites has been made by V. Pöschl,[38] and he has also measured the hardness of the mineral in different directions. As the result of these experiments he concludes that the crystals probably belong to the tetrahedral-pentagonal-dodecahedral sub-class of the cubic system. In the course of the investigation specimens from Elba, from Huttenberg, Carinthia, and from Seegraben in Styria were analysed. The composition of the specifically lightest and heaviest crystals from each locality was determined, but although the density varied by as much as 0·05, no essential difference in composition could be detected. All the specimens contained arsenic, ranging from 0·78 to 1·73 per cent., and copper from 0·04 to 0·63 per cent.

In order to obtain information as to the state of oxidation of the iron in this mineral, G. W. Plummer has heated it to 250° with carbon tetrachloride in a sealed tube. Under these conditions 75 per cent. of the iron is obtained in the ferrous state. He has also found that it is readily decomposed by fusion with bismuth trichloride in an atmosphere of carbon dioxide, all the iron remaining in the ferrous state. He therefore concludes that the whole of the iron is ferrous. This view is supported by the experiments of L. Benedek,[39] who has found that when heated to redness in an atmosphere of carbon dioxide, pyrites loses half its sulphur, ferrous sulphide being left.

Pyrargyrite.—J. Loczka[40] has analysed the crystals from

[34] *Arch. Sci. phys. nat.*, 1911, [iv], **31**, 211, 322, 439, 516; *A.*, ii, 733.
[35] *Ibid.*, and also *Tsch. Min. Mitt.*, 1910, **29**, 498.
[36] B. S. Butler and W. T. Schaller, *Amer. J. Sci.*, 1911, [iv], **32**, 422.
[37] *Bull. Acad. Sci. St. Pétersbourg*, 1911, 897; *A.*, ii, 1104.
[38] *Zeitsch. Kryst. Min.*, 1911, **48**, 572; *A.*, ii, 208.
[39] *Ibid.*, 1910, **48**, 447; *A.*, ii, 44.
[40] *Ann. Mus. Hung.*, 1911, **9**, 318.

Nagybánya, Hungary, which have been described by K. Zimányi.[41] The results are as follows:

S.	Ag.	Cu.	Fe.	Sb.	As.	Total.	Sp. gr.
17·82	59·82	0·07	0·12	22·00	0·08	99·91	5·851

Riebeckite.—Long, black, prismatic crystals intergrown with ægirite occur in pegmatite in the Quincy granite of Massachusetts.[42] The cleavage angle is 55°5′. The optic axial plane is perpendicular to 010, and the acute negative bisectrix inclined 4—5° with the long axis of the prism. The mineral is intensely pleochroic. The composition of the specimen conforms to the type

$$Na_2Fe_2Si_4O_{12},R_4Si_4O_{12},$$

but only contains 42 per cent. of the first of these two molecules. It therefore resembles the specimens from New Hampshire and Colorado rather than the original mineral from Socotra.

Rhodizite.—In 1909 an analysis, by Pisani, of this rare substance from Madagascar was published by Lacroix.[43] Two large crystals from Ampakite, Madagascar, have recently been examined, and a portion of one of them has been found to have the composition $B_{14}Al_6Gl_7(Li,K,Cs,Rb,Na,H)_4O_{39}$, the percentages obtained differing considerably from those found by Pisani. The crystals are pseudo-cubic, being apparently rhombic dodecahedra, showing small faces of two complementary tetrahedra.[44]

Rinneite.—An analysis of carefully selected material from Hildesia confirms the formula $FeCl_2,3KCl,NaCl$, given to the original mineral from Wolkramshausen.[45] It can be prepared artificially in rhombohedral crystals, and is to be regarded as a triple salt, and not as an isomorphous mixture. An experimental investigation of the conditions under which iron salts occur in the Prussian potash-salt deposits has been carried out by H. E. Boeke, the discoverer of rinneite. He has studied the crystallisation of solutions of ferrous chloride and magnesium chloride, of ferrous chloride and potassium chloride, and of the three chlorides together, and deduced the equilibrium diagrams.[46]

Schwartzembergite.—This substance has hitherto been regarded as an oxychloriodide of lead crystallising in the rhombohedral system. A recent investigation [47] of material from the San Rafael mine, Sierra Gorda, Chili, has, however, shown that the crystals

[41] *Ann. Mus. Hung.*, 1911, **9**, 251.

[42] C. Palache and C. H. Warren, *Amer. J. Sci.*, 1911, [iv], **31**, 533; *A.*, ii, 614.

[43] *Ann. Report*, 1909, 217.

[44] L. Duparc, M. Wunder, and R. Sabot, *Bull. Soc. franç. Min.*, 1911, **34**, 131; *A.*, ii, 1105.

[45] F. Rinne and R. Kolb, *Centr. Min.*, 1911, 337; *A.*, ii, 613.

[46] *Jahrb. Min.*, 1911, i, 48; *A.*, ii, 293.

[47] G. F. Herbert Smith and G. T. Prior, *Min. Mag.*, 1911, **16**, 77; *A.*, ii, 1100.

are tetragonal, and that the iodine is present, not as iodide, but as iodate. The analytical results are in agreement with the formula $3(PbCl_2,2PbO),Pb(IO_3)_2$.

Stibiotantalite.—In certain analyses of this mineral[48] tantalum and columbium were estimated by taking the specific gravity of the mixed oxides on the assumption that this property is a linear function of the composition. Recent researches[49] show, however, that this is not quite the case, and a correction amounting to about 2 per cent. must be applied to those analyses.

Strüverite.—This interesting mineral, originally described by Zambonini and Prior, from Craveggia, Piedmont, has recently been found in abundance in a pegmatite vein in the Black Hills of South Dakota.[50] The small, black crystals resemble columbite in appearance, and are tetragonal, with angles near those of rutile. The mineral was completely decomposed on fusion with sodium hydrogen sulphate, but owing to the difficulties attending the separation of columbium, tantalum, and titanium somewhat different results were obtained by different methods. The mean result approximates to the formula $FeO,(Ta,Cb)_2O_5,6TiO_2$. The mineral contains more tantalum than the original strüverite, to which Prior gave the formula $FeO,(Ta,Cb)_2O_5,4TiO_2$.

Thaumasite.—This curious mineral, hitherto only recorded from Sweden and from New Jersey, has lately been observed in fissures in metamorphosed dolomitic limestone in Beaver County, Utah.[51] The composition of the pure white material agrees with the accepted formula, $3CaO,SiO_2,SO_3,CO_2,15H_2O$. Its specific gravity has the remarkably low value 1·84.

Tilasite.—In 1895 H. Sjögren described a massive mineral of the composition $(MgF)CaAsO_4$. Pale green crystals of the same formula have been found recently in manganese ore at Kajlidongri, Jhabua State, India, and have been subjected to a thorough examination by G. F. Herbert Smith and G. T. Prior.[52] It would seem probable that the curiously developed and often twinned crystals belong to that class of the monoclinic system which only exhibits symmetry about a plane: $a:b:c=0{\cdot}7503:1:0{\cdot}8391$; $\beta=59°01\frac{1}{2}'$. The optical characters agree with those determined by Sjögren, an acute negative bisectrix emerging perpendicular to the good cleavage face $\bar{1}01$, the optic axial angle being large, $2V=82°44'$, and the plane of the axes perpendicular to 010. The refractive indices are $\alpha=1{\cdot}640$, $\beta=1{\cdot}660$, $\gamma=1{\cdot}675$(Na). D 3·77.

[48] *Ann. Report*, 1906, 326.
[49] W. E. Ford, *Amer. J. Sci.*, 1911, [iv], **32**, 287; *A.*, ii, 1104.
[50] F. L. Hess and R. C. Wells, *ibid.*, **31**, 432; *A.*, ii, 499.
[51] B. S. Butler and W. T. Schaller, *ibid.*, 131; *A.*, ii, 209.
[52] *Min. Mag.*, 1911, **16**, 84; *A.*, ii, 1103.

Variscite.—W. T. Schaller[53] has found that the bright green, orthorhombic crystals of this substance from Lucin, Utah, have the usual formula, $Al_2O_3,P_2O_5,4H_2O$.

Zeolite Group.—A very large number of analyses of members of this group have been published during the year. As none of them has led to results of special novelty or importance, it will suffice here to refer to the work of E. F. Smith[54] and F. A. Canfield.[55]

Meteorites.

Among the numerous investigations of these substances carried out during the year, several of a general character claim attention. The first of these is the attempt made by O. C. Farrington[56] to apply to the stoney meteorites the system devised in America for the classification of igneous rocks. With this object in view Farrington has made a critical compilation of the published analyses of these meteorites. In fitting them into the classification, certain modifications of the latter become necessary, for regional names cannot be used for designating orders, sections, etc. Accordingly, a group name is assigned to the sub-range only, the name chosen being that of a meteorite which may be considered typical. Further, the presence of uncombined metal in the meteorites necessitates the formation of several new sub-classes. Most of the meteorites fall outside the groups of terrestrial rocks, but Juvinose, Udenose, Stawropolose, Bishopvillose, and Bustose among meteorites correspond respectively with Kedabdekase, Wehrlose, Argeinose, Maricose, and Websterose among igneous rocks. The minerals of meteorites are divided into two groups, salic and femic. The former includes quartz, leucite, felspar, and nepheline; the latter pyroxene, olivine, magnetite, apatite, troilite, oldhamite, schreibersite, and nickel-iron. The methods of calculation employed and the mode of interpreting the analyses are fully set forth in Farrington's memoir.

The distribution of the elements in meteorites and the structure of these substances have been discussed by Wahl.[57] He points out that whereas many meteoric irons have been discovered long after their fall, this is not the case with the stoney meteorites, which are liable to escape detection altogether, unless their fall is actually observed.

If this is not kept in mind false estimates as to the relative

[53] *J. Washington Acad. Sci.*, 1911, **1**, 150; *A.*, ii, 1103.
[54] *Proc. Acad. Nat. Sci. Phil.*, 1911, **62**, 538; *A.*, ii, 501.
[55] *School Mines Quart. New York*, 1911, **32**, 215.
[56] *Field Museum of Natural History. Publication* 151, *Geol. Series*, 1911, **3**, 195.
[57] W. A. Wahl, *Zeitsch. anorg Chem.*, 1910, **69**, 52; *A.*, ii, 47.

importance of iron in meteorites may easily be framed. The presence of easily oxidisable minerals, such as nickel-iron, troilite, etc., and the complete absence of those containing hydroxyl is especially characteristic of meteorites; their magmas were in fact "dry melts," and may be compared with those of basic rocks. The only terrestrial irons which can be compared with meteoric irons are those from Disco, and they contain more carbon and more oxygen than are met with in any meteoric iron.

Speaking generally, it may be said that meteorites and their component minerals differ from terrestrial minerals and rocks in containing a smaller amount of oxygen, and the meteorites themselves may be classified according to their degree of oxidation. The presence of nickel in the metallic part of meteorites and its absence from the olivine is explained by the fact that the heat of formation of nickel oxide is lower than that of iron oxide. When all the available oxygen is exhausted, any calcium left unoxidised unites with the sulphur present to form oldhamite, CaS. If there is enough sulphur, iron sulphide is next formed. The sulphides of cobalt and nickel are not met with, as their heats of formation are less than that of iron sulphide.

These considerations combined with a study of the structure of meteorites leads to the conclusion that the meteorites are small parts of larger bodies, and underwent various changes while still belonging to these larger bodies. The composition of these larger bodies was probably similar in all cases, the different varieties of meteorites coming from different zones. The achondrites and siderolites represent the solidified interior portions, and may be compared with the deep-seated igneous rocks. The chondrites come from the outer layers, and correspond to some extent with terrestrial eruptive rocks.

Some experiments on the synthetical production of meteoric iron have been made by Benedicks.[58] He finds that alloys of iron with 12 per cent. of nickel, prepared by the alumino-thermic process and cooled very slowly below 350°, have a structure which very closely resembles that of the octahedral irons. On the other hand, Ovifak iron resembles a high-carbon steel, and contains free cementite and pearlite, a substance not found in meteoric iron.[59] The atomic weight of the iron of a meteorite from Mexico has been determined, and the results found to agree exactly with those obtained by similar methods for ordinary iron.[60]

[58] C. Benedicks, *Metallurgie*, 1911, **8**, 85; *A.*, ii, 495.

[59] *Ibid.*, 65; *A.*, ii, 287.

[60] G. P. Baxter and T. Thorvaldson, *J. Amer. Chem. Soc.*, 1911, **33**, 337; *A.*, ii, 288.

The composition of taenite has been discussed by O. C. Farrington.[61] It would appear to vary between Fe_7Ni and FeNi.

The question as to the origin of the curious glasses known as moldavite, billitonite, etc., still continues to arouse much interest. On the one hand, their extra-terrestrial origin is maintained, and they are classed together as a special group of meteorites under the name of tektites; on the other, they are regarded as obsidian or volcanic glasses. Several contributions to our knowledge of these objects have been made recently. R. Beck[62] has analysed the gases enclosed in tektites, and has compared them with those obtained from obsidian. The former are distinguished by the presence of considerable quantities of oxides of carbon and by the absence of free chlorine and hydrochloric acid. Certain small beads found in prehistoric burial places in Bohemia have been found on analysis to consist of a highly basic glass.[63] As an artificial origin for these objects seems highly improbable, and as their composition is quite different to that of any known natural glass, it is suggested that they probably belong to the class of tektites.

One of the principal arguments relied on by the upholders of the meteoric theory is the peculiar character of the surface markings of tektites. It would appear, however, that certain glasses found in America exhibit very similar markings to those of moldavite and billitonite.[64, 65] In the light of these observations the case for the meteoric origin of the tektites becomes less convincing than it was.

Among individual meteorites which have been examined lately we may note the following:

Dokáchi.—In 1903 a number of meteoric stones fell in the neighbourhood of Dokáchi, Decca district of Bengal. The examination of one of the smaller of these has shown it to consist of a finely granular mixture of olivine and bronzite with irregular grains of nickel-iron and traces of troilite. Analyses have been made of the nickel-iron and of the silicates attacked by hydrochloric acid, as well as of the silicates undecomposed by that acid.[66]

El Nakhla.—This meteorite fell recently near Alexandria, and is said to consist largely of fragments of hypersthene.[67] As several analysts have been at work on it, further communications may be expected in the near future.

[61] *Field Museum Nat. Hist. Pub.* 145, *Geol. Ser.*, 1910, **3**, 165.
[62] *Monatsber. Deutsch. Geol. Ges.*, 1910, **3**, 240; *A.*, ii, 292.
[63] E. Weinschenk and H. Steinmetz, *Centr. Min.*, 1911, 231; *A.*, ii, 501.
[64] G. P. Merrill, *Proc. United States Nat. Museum*, 1911, **40**, 481.
[65] B. Ježek and J. Woldřich, *Bull. Intern. Acad. Sci. Bohême*, 1910, 15.
[66] H. E. Clarke and H. L. Bowman, *Min. Mag.*, 1911, **16**, 35; *A.*, ii, 616.
[67] S. Meunier, *Compt. rend.*, 1911, **153**, 785; *A.*, ii, 1106.

Leighton.—A stone weighing 877 grams fell in 1907 near Leighton, in Colbert Co., Alabama. It is a grey chondrite.

Quinn Canyon.—A mass of iron weighing 1450 kilos. was found in 1908 near the Quinn Canyon Mountains, Nye Co., Nevada. It is a medium octahedrite, and contains 7·33 per cent. of nickel.

O. C. Farrington,[68] who has described the two meteorites last mentioned, has also given a complete list of all the meteorites found in the United States.

A. HUTCHINSON.

[68] *Field Mus. Nat. Hist., Pub.* 145, *Geol. Ser.*, 1910, **3**, 165; *A.*, ii, 407.

RADIOACTIVITY.

Theories of the Elements.

A STRUCTURAL theory of the atomic weights of the elements has been put forward [1] which has a definite theoretical foundation, and is certainly in surprisingly good accord with the best chemical determinations. The underlying idea is to regard the whole mass of an atom as of purely electromagnetic origin due to the presence of equivalent charges of positive and negative electricity. The latter are the well-known negative electrons, which, as is now generally admitted, can only represent an insignificant fraction of the total mass of any atom. The unknown positive charges are therefore regarded as existing in units excessively small in radius compared even with the radius of the negative electron, and since the inertia, or mass, is proportional to e^2/a, where e is the charge and a is the radius, the mass contributed by the positive charges is so increased until it represents nearly the total atomic mass. In other words, the unit positive charge is regarded as an entity as much smaller than the negative electron as the latter is smaller than the atom. Sir J. J. Thomson's original view that the positive electricity has a uniform volume distribution is, however, retained, and is essential. The author then constructs four primary atoms or "protyles," out of which all atoms are built up. The single electron, with its equivalent single concentrated positive charge, cannot exist, but for systems, respectively, of two, three, four, and five negative electrons, in rings at equidistant intervals round a single equivalent concentrated positive charge, permanence may be assumed, as in such ring systems the vector sum of the accelerations towards the centre is zero, and the drain on the kinetic energy of the system due to radiation is null. Quite definitely, then, in this conception, the positive charge is a single sphere of *uniform volume distribution* of from 2 to 5 atomic charges of positive electricity. The radius of this sphere is therefore proportional to $n^1/^3$, where n is the number of atomic charges. The inertia or mass, which is, as already stated, practically the whole atomic mass, being pro-

[1] J. W. Nicholson, *Phil. Mag.*, 1911, [vi], **22**, 864; *A.*, 1912, ii, 35.

portional to e^2/a, is proportional to $n^2/n^{1/3}$, that is, to $n^{5/3}$, so that the atomic weights of the four protyles are, neglecting, as is permissible, the mass of the negative electrons, in the ratio of the numbers 2, 3, 4, and 5 raised to the 5/3rds power. The first of these is taken to be coronium (Cn), the second, hydrogen, the third, nebulium (Nu), and the last, protofluorine (Pf). It must be mentioned that it is not definitely postulated that hydrogen is a single three-electron ring system, but possibly may be some multiple of such a system, presumably not a large multiple, with corresponding changes in the structure of the other protyles. Hence the radius of the positive sphere of electrification is left indefinite. Taking the atomic weight of hydrogen as 1·008, the relative atomic weights of the others, corrected for the mass of the equivalent negative electrons, are:

Cn 0·5131 Nu 1·6277 Pf 2·3604.

Only the two latter and hydrogen enter into the composition of the known elements, coronium being regarded, on account of its simple structure, as less stable. It is stated that the spectra of coronium and protofluorine in the solar corona, and of nebulium in nebulæ, give mathematical justification for the structures assigned, but unfortunately this interesting point is not discussed further in the paper. The structure of the elements of atomic weight below 25, and it is only these in which the chances of accidental coincidence is small, is then represented in the second column of the following table. The third column represents the atomic weight calculated from the structure, and the last that given in the International List:

Helium	NuPf	3·988	3·99
Lithium	? H_2Nu_3	6·90	6·94
Glucinum	H_2Pf_3	9·097	9·10
Boron	H_3He_2	11·00	11·00
Carbon	H_4He_2	12 008	12·00
Nitrogen	H_6He_2	14·02	14·01
Oxygen	H_4He_3	15·996	16·00
Fluorine	H_7He_3	19·02	19·0
Neon	H_6Pf_6	20·21	20·2
Sodium	H_7He_4	23·008	23·00
Magnesium	H_2He_5Pf	24·32	24·32

The structures assigned appear somewhat arbitrary, but the coincidence between the calculated and the determined atomic weight, except in the case of lithium, is extraordinary. It is curious to note that the approximation to whole numbers of the atomic weights nowhere enters explicitly into this scheme, but would appear to be an accidental consequence of the values of the five-third powers of the numerals 3, 4, and 5, and the unit chosen for oxygen. The underlying theoretical idea is commendably

definite and simple, but its further development in the paper is very open to criticism. For example, the author is at pains to construct three new inert gases having positions in the Periodic Table between cobalt and copper, palladium and silver, platinum and gold, which surely is in violation of all probability. Again, the evidence that the α-particles of the radio-elements differ only in the initial velocity of their expulsion, which has been discussed fully in these Reports, appears to be largely unknown to the author, who regards it as "not in opposition to any phenomena known with certainty" that the α particles from different sources may consist of different atoms. Whereas in most cases separate determinations of the velocity and of the ratio of the charge to the mass are available. Some of the radioactive evidence cited is well known to be erroneous; for example, the statement that the α-rays of polonium and radium are equally deviated in the magnetic field.[2] Apparently there is a difficulty in obtaining satisfactory constitutions for the radio-elements which shall exhibit them as successive transformation products by losses of helium atoms, whereas one of the most interesting features from the radioactive point of view of the structures assigned to the lighter atoms in the table given is the predominant part assigned to helium.

The attempt has been made[3] to revive the cubic periodic system, once proposed by Mendeléeff to accommodate the rare gases, the new rare earths, and the disintegration products of radioactive elements. The feature of this proposal is that 120 possible places are assigned to the elements, excluding hydrogen, which are arranged in eight families, each containing fifteen places in sub-families of five, the first member of the family being placed above the fourth, the second above the fifth, and so on. It is pointed out that on this system the sum of all the known atomic weights is within 0·3 per cent. of the calculated value, on the assumption that the atomic weight increases 2 units, or half the atomic weight of the α-particle, regularly in passing from one place to the next in the system. The system, it is claimed, accommodates all the known α-ray-giving radio-elements. These exactly fill the vacant places. However, it may be pointed out that two new members have since been recognised, and that in this system many of the very definite analogies between the elements, which are brought out in the ordinary arrangement, are no longer recognisable. In another system,[4] attempts are made to build up the atomic weights out of the two series $4n$ and $4n-1$, when n is an integer, an arrange-

[2] Compare *Ann. Report*, 1906, 334.

[3] A. van der Broek, *Physikal. Zeitsch.*, 1911, **12**, 490; *A.*, ii, 709.

[4] T. Wulf, *Physikal. Zeitsch.*, 1911, **12**, 497; *A.*, ii, 709.

ment due originally to Rydberg as far back as 1886, who pointed out that the elements possessing even valency fall in the first series, and those with odd valency fall in the second series mentioned. This would accord well with the idea that helium, or the α-particle, is a fundamental unit in the structure of atoms. About forty elements have atomic weights in near accord with this view, the numbers corresponding with each of the two series being equal.

α-Rays.

The scattering of α-particles in their passage through the atoms of matter[5] possibly will give an experimental means of learning something of the nature of the atomic structure. The passage of the α-particle through the atoms of matter is the only known phenomenon for which the dictum that two particles of matter cannot occupy the same space at the same time is not true, so that it is not unreasonable to hope that, after such passage, the α-particle may bear some evidence of what is inside of the otherwise impenetrable atoms it has traversed. A small fraction of the incident α-particles, about 1 in 20,000, is turned through an angle of 90° by impact on a gold leaf 0·00004 cm. thick, whereas the most probable angle of scattering is, under the same conditions, less than a degree. It is necessary to suppose that such large deflexions cannot be, as has hitherto been imagined, the result of a multitude of successive small scatterings, for the chance of numerous successive encounters, the effects of which all assist rather than cancel out one another, must be very small. The view that they are the result of single encounters of necessity leads to the view that the atom is the seat of a much more intense electric field than in Sir J. J. Thomson's theory of the atom, in which the sphere of uniform positive electrification is supposed to possess atomic dimensions. That is to say, as in the theory of atomic weights previously discussed, a concentrated central charge is postulated, the effects of the outer less concentrated equivalent opposite charge being neglected. Preliminary measurements of the scattering suffered by the α-particle confirm the general correctness of the theory worked out on this basis. On the other hand, the theory involves the consequence that, whereas in an encounter with a heavy atom, like that of gold, the loss of energy of the α-particle should be small, in the case of a light atom, such as aluminium, the loss would be considerable, whilst in the case of a hydrogen atom it would appear that in certain cases a more or less complete exchange of energy should occur. These cases, however, have not yet been investigated.

[5] E. Rutherford, *Phil. Mag.*, 1911, [vi], **21**, 669; *A.*, ii, 453.

From previously published results [6] on the scattering with platinum, the magnitude of the central charge of the platinum atom is deduced to be about $100e$. For different metals, if the magnitude of the central charge is proportional to the atomic weight, it is deduced that the relative scattering should be proportional to the two-thirds power of the atomic weight, and this agrees with the experiments published. The results of Crowther with β-rays [7] are also shown to be in general accord with the theory. The most important change brought about by these experiments is the substitution of a concentrated central charge of considerable magnitude for the uniform sphere of electrification, of dimensions comparable with the atomic diameter, hitherto generally assumed. This conception differs again from the one previously discussed, in that a single central charge is postulated, whereas on the other view, although the constituent protyles are given single charges, in the coalescence of these protyles into atoms, the central charges do not coalesce, but, at least to some extent, retain their identity. The latter view renders easier the comprehension of the main radioactive process, the expulsion of a helium atom, which, it is only reasonable to conclude, has existed in the parent atom previously, to a certain extent at least, as a distinct entity, before it is expelled.

α-Rays of Uranium.—Special interest centres around the α-rays of uranium. If the two α-particles, known to be given out per atom of uranium in its first change, are not given out simultaneously, the so-called element uranium must consist of a mixture of two elements, differing in atomic weight by 4 units, in a relative proportion the same as the relative periods of the two elements, and, as in so many other cases now known, non-separable by chemical methods.[8] It is altogether unlikely, in view of the low range of the uranium α-particles, which is the lowest known, that the period of the element of lower atomic weight can be less than that of ionium, the element giving α-rays the next lowest in range. The proportion therefore of the element of lower atomic weight cannot therefore be entirely insignificant, although it may not be more than some grams to the ton as the minimum. On the other hand, there is no reason why it should not be a considerable proportion of the whole.

The question whether the two α-particles of uranium can be expelled simultaneously or with only short average intervals, up to a few seconds, between them seems to have been definitely decided in the negative by observations of the scintillations from a layer of uranium oxide enclosed between two zinc sulphide screens,

[6] *Ann. Report*, 1909, 237.
[7] *Ibid.*, 1910, 266.
[8] Compare *ibid.*, 1909, 259.

observed by two observers with microscopes focussed on opposite portions.[9] Under these conditions, pairs of simultaneous scintillations were not observed, neither was there any preponderance of short intervals between the scintillations beyond that required by the theory of probabilities for a random distribution of intervals.

On account of the shortness of their range, it is difficult to decide by the usual methods whether the α-rays of uranium are homogeneous. A new determination has been made by placing a zinc sulphide screen centrally within a spherical glass flask of 10 cm. diameter, internally coated with a thin layer of uranium salt, and counting the number of scintillations on the screen by the aid of a lens outside the flask, for various pressures of air in the apparatus.[10] The range so determined at ordinary temperature corresponded with 2·68 cm. of air, which is in agreement with other recent determinations; but a sharp change in the direction of the curve, at a point corresponding with about half this range, indicates that the radiation may not be homogeneous. Evidence of the same character was also obtained by photography. A photographic film placed behind a zinc sulphide screen inclined to a flat surface of uranium showed evidence of a decided change of density at the point where the α-particles would travel about one-half of their complete range. If these results are confirmed, and it is proved that two sets of α-particles are emitted, one with a range only one-half of the other, it is to be expected that the element of lower atomic weight with the α-rays of greater range would possess a period of the order of only some millions of years, and that its relative quantity, although not negligible, will hardly be sufficient seriously to affect the determined atomic weight of uranium. There are, however, grounds for not accepting this result without further confirmation.

Ranges of α-Rays.—A new set of determinations of the ranges of various α-particles has been carried out by the ionisation method.[11] A film of the active substance was supported centrally in a globe internally silvered, and the ionisation current through the gas plotted against the pressure of the gas. From the pressure at which the α-rays just reach the walls of the flask, upward, the ionisation is constant, but at this pressure there is a sharp point of inflexion, and the ionisation at lower pressures is proportional to pressure. The following table shows the results obtained with the uranium series. The temperature appreciably affects the range by affecting the density of the air, and the results have therefore been calculated for both 15° and 0°. The last column gives the calculated initial

[9] E. Marsden and T. Barratt, *Proc. London Phys. Soc.*, 1911, **23**, [v], 367; *A.*, 1912, ii, 6. Compare *Ann. Report*, 1910, 257 and 258.

[10] A. Foch, *Le Radium*, 1911, **8**, 101; *A.*, ii, 354.

[11] H. Geiger and J. M. Nuttall, *Phil. Mag.*, 1911, [vi], **22**, 613; *A.*, ii, 953.

velocity of the α-particle. The ranges are expressed in cm. of air under 760 mm. pressure:

	Range (15°).	Range (0°).	Initial velocity $\times 10^9$ cm./sec.
Uranium	2·72	2·58	1·51
Ionium	3·00	2·84	1·56
Radium	3·30	3·13	1·61
Polonium	3·77	3·58	1·68
Thorium	2·72	2·58	1·51
Radiothorium	3·87	3·67	1·70

The result for uranium confirms the value of the range found in the preceding investigation, but no evidence was obtained pointing to the existence of a second set of α-rays of lower range.

It has long been known that, with a few apparent exceptions, the longer the range of the α-rays the shorter is the period of the substance. That a mathematical relationship of some kind exists between the range and the period is shown by plotting the logarithms of the ranges (or of the velocities, which are proportional to the cubes of the ranges) against the logarithms of the periods. For those members for which both points are known in the uranium series a straight line results. If ionium, for which the range, but not the period, is known, is placed on this line, the period corresponding with the range is nearly a million years. For the α-ray-giving product of radium-*C* the period calculated from the range of the rays is only one-millionth of a second. A similar straight line relation holds in the actinium series, the line being parallel to that in the uranium series, the ranges for corresponding periods being, however, somewhat higher.

An interesting new method for making visible the track of the individual α-rays, and also of the β-rays, through a gas is to condense water-drops on the ions left behind in the paths of the rays.[12] As is well understood, the velocity of these rays is such that the gas molecules may be considered to be at rest by comparison. At the instant the α-particle passes there is formed a cylindrical column of ions in its track, of a diameter not greatly different from the molecular diameter and of length corresponding with the range of the particle. This "columnar" ionisation with α-rays and the great concentration of the ions within the columns well explains the phenomenon of initial recombination encountered with α-rays.[13] The apparatus employed to render these columns visible is a cylindrical expansion chamber, with flat, horizontal roof and floor of glass, coated with gelatin to render it electrically conducting and to prevent the formation of dew. The gelatin on the floor is blackened with Indian ink to form a dark background. The α-rays

[12] C. T. R. Wilson, *Proc. Roy. Soc.*, 1911, A, **85**, 285; *A.*, ii, 565.

[13] *Ann. Report*, 1909, 238.

may be derived from the radium-tipped point of a spinthariscope within the chamber. An electric field between the roof and floor keeps the chamber clear of ions up to the moment of expansion. On expansion the individual tracks of the α-particles are clearly seen on the dark background of the floor, when the chamber is brightly illuminated. By illuminating the chamber with a powerful spark, from 0·1 to 0·2 second after expansion, these tracks may be photographed. Some of the tracks are remarkably sharply defined lines. Others show a doubling due to the incipient separation of the positive and negative ions by the field. With β-rays the straight thread-like tracks, due to the primary rays radiating from the source, are crossed by others, due to secondary rays from the walls of the chamber. In the ionisation produced by γ-rays the large part played by β-rays is brought out, whilst with *X*-rays the thread-like tracks are rarely straight, but often have a beaded structure, which is perhaps due to the zigzag paths of the very low velocity β-rays generated by *X*-rays. The evidence favours the view that γ- and *X*-ray ionisation is entirely an affair of the β- and cathode rays they produce, and hopes are entertained that a definite proof of this difficult point may be reached by the new method.

It has been established, by experiments with the α-particles emitted from a radioactive solution, that the von Schweidler variation is much greater in this case than in that of the α-rays from a solid preparation, a phenomenon which is to be expected on the present kinetic theory of the incessant violent motions possessed by the individual molecules of a liquid. The Brownian movements of small suspended particles merely render this commotion visible, but it occurs universally, and to the same degree both in the liquid and gaseous states. Superimposed on the ordinary variation in the actual number of α-particles emitted in a short time-interval is a second variation due to momentary changes of concentration of the radioactive molecules in the liquid, produced by their own unco-ordinated movements.[14]

Helium.

A careful and accurate measurement[15] of the quantity of helium produced from a known quantity of radium, nearly 0·2 gram of the chloride, during periods of eighty-three and one hundred and twenty-eight days, agreed in giving as the result that 0·156 c.c. of helium, at N.T.P., is formed every year per gram of radium (element) in equilibrium with its first three α-ray-producing products. This figure is subject to correction when an accepted

[14] T. Svedberg, *Arkiv. Kem. Min. Geol.*, 1911, **4**, No. 22.

[15] B. B. Boltwood and E. Rutherford, *Phil. Mag.*, 1911, [vi], **22**, 586; *A.*, ii, 953.

standard of pure radium is available, the specimen employed being 97·22 per cent. in terms of the Royal Society's radium. The theoretical rate, calculated from the number of α-particles expelled, which is $1{\cdot}36 \times 10^{10}$ per gram per second, is 158 cu.mm. per year, assuming that helium has a monatomic molecule. The number of molecules in a c.c. of gas under standard conditions deduced with a minimum of assumption from these results is $2{\cdot}69 \times 10^{19}$, and the value of Avogadro's constant, or the number of molecules in the mole of any gas, is almost exactly 7×10^{23}.

A preparation of ionium,[16] weighing 1·8 grams, and of α-activity 3000 times uranium, in one hundred and twenty-five days generated 0·031 cu.mm. of helium. This is little more than half the theoretical amount (0·0595 cu.mm.) calculated from the number of α-particles expelled, but the helium was removed by ignition of the preparation in a Jena-glass tube, and some may have been retained. Similarly with a polonium preparation,[17] initially of amount equal to that in equilibrium with 4·1 milligrams of radium, the observed production of helium, 0·009 cu.mm. in one hundred and twenty-eight days, is only about one-fourth of the calculated value. Here undoubtedly a part of the helium would embed itself in the copper plate on which the polonium was deposited.

The red fluorspar of Ivitgut, Greenland,[18] was separated from the adjacent cryolite, and divided into a lighter and heavier fraction. The lighter part contained 4 per cent. of rare earths, including thoria and the helium. The heavier part consisted of an iron and copper mineral containing uranium and lead. The conclusion was drawn that the fluorspar, but not the cryolite, is able to absorb and retain the helium. Similarly, helium has been detected in the insoluble matrix in which Portuguese autunite occurs, after the mineral has been dissolved out by acid.[19] The gas evolved by ignition was estimated to contain about the same amount of helium as the gas evolved on solution of the original mineral in acids. The conclusion was drawn that the purer autunite is, and the less earthy matrix mixed with it, the less helium it contains, and therefore that the helium content is not connected with the age of the mineral. It is possible, of course, that a radioactive mineral may be permeable to the helium produced within it and be encased in a matrix which is not so permeable, with the result that the matrix, but not the mineral, may be found to contain helium; but the attempts which have been made to show that

[16] B. B. Boltwood, *Proc. Roy. Soc.*, 1911, A, **85**, 77; *A.*, ii, 359.

[17] B. B. Boltwood and E. Rutherford, *Phil. Mag.*, 1911, [vi], **22**, 586; *A.*, ii, 953.

[18] *Ann. Report*, 1907, 323; Hans Lange, *Zeitsch. Naturwiss. Halle*, 1910, **82**; *A.*, ii, 499.

[19] A. Piutti, *Le Radium*, 1911, **8**, 204; *A.*, ii, 565.

substances may selectively absorb helium, so vitiating this method of estimating geological age, are unconvincing.[20]

β-Rays.

Important developments have occurred in connexion with the nature of the β-rays. The determination of the magnetic spectrum[21] under proper conditions has established that the apparent heterogeneity of, for example, the β-rays of the radium active deposit originating in the disintegration of radium-*B* and -*C* is due, in the first place, to the existence of a large number of separate types of rays each homogeneous as regards velocity when expelled, and, in the second place, to the conversion of these initially homogeneous rays into heterogeneous rays when they traverse any absorbing material. The main idea, therefore, that in each disintegration the β-particles, like the α-particles, are expelled with definite characteristic velocities, is borne out, but the further view that a single disintegration gives only one homogeneous type of rays, and that, therefore, a complex radiation is evidence of a complex series of changes, is not substantiated.

The effect of absorbing screens on the velocity of β-rays seems to depend on the magnitude of the velocity of the rays. The slower β-rays, moving at a velocity up to, perhaps, 70—80 per cent. of that of light, in passage through an absorbing medium suffer reduction of the velocity as a whole without loss of homogeneity, and therefore there is no difficulty with them in obtaining fairly sharp lines in the magnetic spectrum. The β-rays moving with velocities greater than these usually appear as heterogeneous, and neither their velocity nor their degree of heterogeneity is altered by passage through absorbing screens.[22]

Of the first class of low-velocity rays, radium itself gives two types, of which the velocities, in terms of that of light, have been provisionally estimated to be 0·65 and 0·52.[23] Radium-*B* gives five types of velocities: 0·74, 0·69, 0·63, 0·41, and 0·36.[24] Radium-*D* gives two types of velocities: 0·39 and 0·33.[25] Thorium-*B*[26] gives one type of velocity, 0·63, and there are three other types of velocities: 0·72 (feeble), 0·36, and 0·29, due either to thorium-*B* or -*D*.

[20] *Le Radium*, 1911, **8**, 13; *A.*, ii, 88; R. J. Strutt, *Nature*, 1910, **85**, 6.

[21] Compare *Ann. Report*, 1910, 265.

[22] O. v. Baeyer, O. Hahn, and L. Meitner, *Physikal. Zeitsch.*, 1911, **12**, 273; *A.*, ii, 567.

[23] *Ibid.*, 1099; *A.*, 1912, ii, 7. [24] *Ibid.*

[25] *Ibid.*, and O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1911, **12**, 378; *A.*, ii, 567.

[26] Throughout the new nomenclature (p. 285) is adopted.

The main type of β-rays of thorium-*D* belong to the other class of high-velocity rays, and have not yet been resolved. They appear heterogeneous, with velocity between 0·93 and 0·95.[27] The high-velocity β-rays of radium-*C* are the only ones of the class so far resolved. Four types are present, with velocities 0·98, 0·94, 0·86, and 0·80.[28]

The measurements given of the velocities of the β-rays of radium-*B* and -*C* were done by means of a silver wire coated with the two substances together, and of a nickel wire coated with radium-*C* only, so that no previous absorption of the rays occurred. The priority, however, of resolving the β-rays of radium belongs to an independent investigator,[29] with the radium emanation contained in a capillary glass tube just sufficiently thick in the walls to absorb α-rays. Photographs of the magnetic spectrum showed that the β-rays had been sorted into seven types, the two lowest velocity types of radium-*B* probably not having escaped from the tube. The velocities obtained agree very closely with those given, but the rays due to radium-*B* and -*C* separately were not distinguished.

In a later communication[30] very accurate measurements are given of the seven strong beams given by radium-*B* and -*C* together. Their velocities are: 0·615, 0·682, 0·735, 0·786, 0·862, 0·940, and 0·957. The first four are from radium-*B*, and the last three from radium-*C*, according to the work already discussed. The first three comprise rays differing in velocity about 1 per cent. on either side of the mean velocity, but the others are quite sharp. In addition, no less than fourteen other beams of β-rays, equally definite but comparatively feeble, have been recognised, alternating fairly regularly with the seven strong beams. Also, two other beams of extremely high velocity, and in consequence very difficult to deviate, have been made out. Such β-rays resemble the γ-rays in affecting the photographic plate but feebly. The first beam is complex, and consists of from three to five separate beams, with mean velocity 98·8 per cent. of that of light and value for $H\rho$ (the measure of their magnetic deviability) 11,200. The last beam has the mean velocity no less than 99·6 per cent. and mean value of $H\rho$ 18,100, although for some of the rays 99·8 per cent. and over 26,000 are the figures given. This confirms the work of previous investigators that it is impossible completely to deviate the β-rays of radium, and also of uranium, in a magnetic field, and that some of the β-rays

[27] O. v. Baeyer, O. Hahn, and L. Meitner, *Physikal. Zeitsch.*, 1911, **12**, 273; *A.*, ii, 567; *ibid.*, 1099; *A.*, 1912, ii, 7.

[28] *Ibid.*, 1099; *A.*, 1912, ii, 7.

[29] J. Danysz, *Compt. rend.*, 1911, **153**, 339: *A.*, ii, 840.

[30] *Ibid.*, 1066.

in each case must possess velocities very nearly indeed approaching that of light itself.[31]

The only radioactive substances decomposing truly raylessly are mesothorium-1 and actinium. Most of those at first thought to be rayless, for example, radium-*D* and the -*B* members of the three active deposits, have been shown to give low-velocity β-rays. Some of these β-rays do not surpass in velocity the artificially generated cathode-rays, and in penetrating power are not much superior to the α-rays. To distinguish them from the penetrating β-rays, to which the name was first applied, the symbol "(β)-rays" has been employed.

γ-Rays.

Attempts hitherto made to generate γ-rays by the impact of β-rays of radium on metals, in the same way as *X*-rays are generated from cathode-rays, have not been successful, any such effect being too small to be detected with certainty. By using the β-rays of a preparation of radium-*E*, the γ-rays of which are extraordinarily feeble, such a generation of γ-rays by the β-rays has been put into evidence, although it is feeble. Bringing a radiator of lead under a layer of radium-*E* placed beneath an electroscope, the base of which consisted of sufficient cardboard and aluminium to absorb the β-rays completely, gave an increased leak, and that this was due to the β-rays was shown by covering the upper surface of the radiator with sufficient paper to absorb all or a known proportion of the β-rays, when the increase of the leak in the electroscope was reduced correspondingly. The secondary γ-radiation increases in amount with the atomic weight of the radiator, and is roughly proportional to it. The secondary γ-rays formed are the more easily absorbed the greater the atomic weight of the absorbing metal, as is the case with *X*-rays. It is surmised that the γ-rays of radium-*E* may be entirely of secondary origin, and the suggestion is made that the γ-rays of uranium-*X* may also be secondary. The latter suggestion was made without any examination of the rays in question, and is unfounded.[32]

An investigation of the effect of temperature on the absorption-coefficient of iron for the γ-rays of radium, between 600° and 700° and room temperature, showed that temperature exerts no direct influence. A small diminution of the coefficient, about 0·002 per cent. per degree rise of temperature, is almost exactly what is to be expected from the expansion of the iron with heat and its consequent decrease of density and increase of thickness.[33]

[31] *Ann. Report*, 1909, 241.
[32] J. A. Gray, *Proc. Roy. Soc.*, 1911, A, **85**, 131; *A.*, ii, 355.
[33] W. Wilson, *Phil. Mag.*, 1911, [vi], **21**, 532.

The coefficient of absorption of the γ-rays of radium-*C* in air at 22° and 750 mm. has been experimentally determined to be $0{\cdot}45 \times 10^{-4}$.[34] This constant has an importance in connexion with the earth's penetrating radiation.

δ-Rays.

The view is gaining ground that the electrons, or δ-rays, emitted when a metal plate is struck by α-particles are due to the ionisation of the metallic atoms by a process identical with that which occurs in a gas when α-rays traverse it. The emission of δ-rays from very thin aluminium and gold leaves in a high vacuum has been measured for different parts of the range of the α-particle. The curves connecting the emission of δ-rays and the range of the α-particle are completely analogous in form to the Bragg curve connecting the ionisation in gases and the range.[35] Some points still remain to be cleared up; for example, aluminium and gold showed practically the same curve, whereas, since heavy atoms are more effective in retarding α-rays at the commencement of their path than light atoms,[36] certain differences between the forms of the two curves were anticipated. The similarity between the two metals, which differ so greatly in atomic weight, raises the question whether the δ-particles result from the metal or from a film of condensed gas of the same nature in each case. With the α-rays of thorium-*C*, which are known to comprise two sets of α-rays of greatly different ranges, the δ-ray-range curves showed the two "knees" characteristic of the ionisation-range curve.

Certain negative tentative conclusions with regard to the nature of the δ-rays have been put forward, which, if confirmed, are of great importance in regard to the nature of gaseous ionisation; thus the speed of the δ-particles and their number is apparently independent of the speed of the α-particle and of the nature of the metal from which they are emitted. In this work about 10 δ-particles were emitted per α-particle of polonium.[37] In another research the number 17 was obtained from brass, whereas the copper plate on which the polonium was deposited expelled about 60 δ-particles per α-particle. The kinetic energy of each kind was similar, and their penetrating power was found to be from 1/7th to 1/11th of that of the α-particle of polonium.[38]

[34] V. F. Hess, *Sitzungsber. K. Akad. Wiss. Wien.*, July, 1911, **120**, IIa.
[35] H. A. Bumstead, *Phil. Mag.*, 1911, [vi], **22**, 907; *A.*, 1912, ii, 8.
[36] Compare *Ann. Report*, 1909, 237.
[37] N. Campbell, *Phil. Mag.*, 1911, [vi], **22**, 276; *A.*, ii, 841.
[38] F. Hauser, *Physikal. Zeitsch.*, 1911, **12**, 466; *A.*, ii, 685.

Ionisation.

No claim is made in these reports for anything like a complete account of the progress made in the great subject of ionisation, which is distinct from that of radioactivity although closely connected with it, as to do it, and the similar subject of *X*-rays, justice an unduly large part of the available space would be necessary. Some brief references only can be given.

The view that the ionisation produced by an α-particle is proportional to the loss of energy suffered by the α-particle has been confirmed, but the amount of energy required to produce an ion is not the same for all gases, and varies from 1·01 for hydrogen to 0·73 for carbon dioxide (air being taken as unity). The heavier and more complex molecules are somewhat more easily ionised than the light and simple ones. With regard to β-rays, β-ray-giving products have been selected which can be obtained in equilibrium with an α-ray-giving product. If per α-particle emitted, and therefore per atom disintegrating, only one β-particle resulted in all cases, from measurements of the ionisation and number of α-particles could be deduced the relative ionisation caused per β-particle in the different cases. Or, if it be assumed that in each case the ionisation produced per β-particle is of the same order, then the measurements will afford an idea of the relative number of β-rays expelled per atom of the β-ray-giving substance disintegrating. This line of attack makes it appear that thorium-*D* and actinium-*D* give twice as many β-particles per atom disintegrating as uranium-*X* and radium-*E*, whilst radium-*C* is intermediate.[39] This reasoning as regards thorium-*D* involves the assumption that two α-particles are expelled, one each per atom of thorium-C_1 and -C_2, which has subsequently been shown not to be the case, the two products before supposed to be successive being more probably simultaneous (p. 289). If during the disintegration only one α-particle is expelled per atom of thorium-*B* disintegrating, then both the products thorium-C_1 and -C_2 must give thorium-*D*, in order that that member should expel one β-particle per atom disintegrating, which is an interesting but somewhat improbable conclusion.[40] On the assumption that the radium-*E* atom gives one β-particle, about 67 ions are produced in air per cm. of path per β-particle. In another investigation, in which the same assumption was made for the radium-*C* atom, the number 48 was obtained, or $1{\cdot}2 \times 10^4$ ions in the complete path. On the assumption that one

[39] H. Geiger and A. F. Kovarik, *Phil. Mag.*, 1911, [vi], **22**, 604; *A*, ii, 954; W. Wilson, *Proc. Roy. Soc.*, 1911, A, 85, 240; *A.*, ii, 516.

[40] E. Marsden and T. Barratt, *Proc. London Phys. Soc.*, 1911, **24**, i, 50.

γ-ray, considered as an entity, is evolved from radium-*C* per β-particle, the corresponding numbers for the γ-ray are 1·2 and 3×10^4. If the heating effects and ionisations are proportional, the β-rays contribute 2 calories, the γ-rays 4·5 calories of the total 110 calories emitted per hour per gram of radium.[41]

Wonderful developments have been made in the cloud method of measuring the atomic charge by the use of non-volatile liquids, single droplets of which have been kept under continuous observation for hours, while they from time to time attracted positive or negative charges from the ionised gas, and abruptly altered their velocity under the opposed actions of gravity and an electric field. The mean value, $4{\cdot}9016 \times 10^{-10}$ E.S.U., has been deduced for the atomic charge, the number of such charges on the droplet, which droplet was comparatively large, varying from 4 to 17 during one observation.[42] Arising out of this work the conclusion was drawn that the primary act of ionisation always results in singly charged, or "univalent," ions, and that multiple charges on ions result by subsequent actions, a conclusion which has been called into question.[43] The mass of the gaseous ion has also been the subject of important investigation,[44] whilst a re-investigation of the effect of temperature has shown that even when the mean kinetic energy of translation of the molecule is doubled, its ability to be ionised is not altered by 0·1 per cent.[45] The view that the charge on an ion wanders from molecule to molecule, so that for only a part of the time it is charged, the observed mobility being only a mean value for different charged molecules, has been tested by an ingenious method and been found wanting.[46]

New Short-lived α-Ray Products. Changes of Nomenclature.

The discovery of the existence of double scintillations with the α-rays of the actinium emanation, and of pairs of successive scintillations, at about 0·2 second interval, with the α-rays of the thorium emanation,[47] has now been followed up, and proof obtained that in each case a new α-ray product of the emanation exists in the series intermediate between it and what has hitherto been termed thorium-*A* and actinium-*A*. An examination of the range

[41] A. S. Eve, *Phil. Mag.*, 1911, [vi], **22**, 551 ; *A.*, ii, 956.
[42] R. A. Millikan, *Le Radium*, 1910, **7**, 345 ; *A.*, ii, 175.
[43] R. A. Millikan and H. Fletcher, *Phil. Mag.*, 1911, [vi], **21**, 753 ; *A.*, ii, 573 ; J. S. Townsend, *Phil. Mag.*, 1911, [vi], **22**, 204; *A.*, ii, 686.
[44] J. S. Townsend, *Proc. Roy. Soc.*, 1911, A, **85**, 25 ; *A.*, ii, 355 ; W. Duane, *Compt. rend.*, 1911, **153**, 336 ; *A.*, ii, 839.
[45] J. H. Clo, *Le Radium*, 1911, **8**, 108 ; *A.*, ii, 355.
[46] J. Franck and L. Meitner, *Ber. Deut. physikal. Ges.*, 1911, **13**, 671 ; *A.*, ii, 958.
[47] *Ann. Report*, 1910, 257.

of the α-particle of actinium emanation revealed the existence of two sets of α-rays.[48] The range of the α-ray of the emanation itself is 5·7 cm. of air, that of its evanescent product 6·5 cm., that of actinium-*X* 4·4 cm., and of the actinium active deposit (AcC) 5·4 cm. These values correct previously given values.[49] Using a tube provided with a thin mica window, in which actinium emanation circulated, and containing an electrode so arranged that no α-rays coming from this electrode could escape from the window, it was arranged that only the α-rays of longest range, 6·5 cm., could reach an external screen placed outside the mica window. The application of a field, charging the electrode negatively, instantly resulted in a greatly reduced number of scintillations on the screen, whilst the interruption of the field instantly restored the number to the first value. Hence the evanescent product of the actinium emanation behaves like a non-volatile product of the "active deposit" type, being attracted to a negatively charged electrode. From the field necessary to reduce the number of scintillations to a determined extent, a rough but, as it proved, extraordinary close estimate of the period of the product could be obtained. This was only of the order of 1/500th second.

Two methods of putting into evidence this extraordinarily quick-changing product, and also the similar but less short-lived new product of the thorium emanation, have been devised. An electrode coated with zinc sulphide immersed in either of the emanations instantly glows when made negative with respect to the vessel, and as instantly ceases to glow when discharged. Indeed, the actinium product was observed in a similar manner eight years before.[50] The conclusion was then drawn that the rays from the emanation were attracted by a negatively charged object, and in this respect were peculiar, the name *E*-rays being given to them. Actually, of course, the product attracted to the negative electrode changes, and expels its α-rays so rapidly after deposition that to the unaided eye it appears as if it were the rays themselves, rather than the ray-producing products, which are attracted by the field. By driving with a motor an endless wire, negatively charged, through holes in the ebonite stoppers of a cylinder containing a source of either of the emanations, it can be shown that as long as the motor is working the wire gives out a strong α-radiation as it leaves the cylinder. This activity and its decay as the wire travels from the cylinder can be studied by means of a zinc sulphide screen.[51]

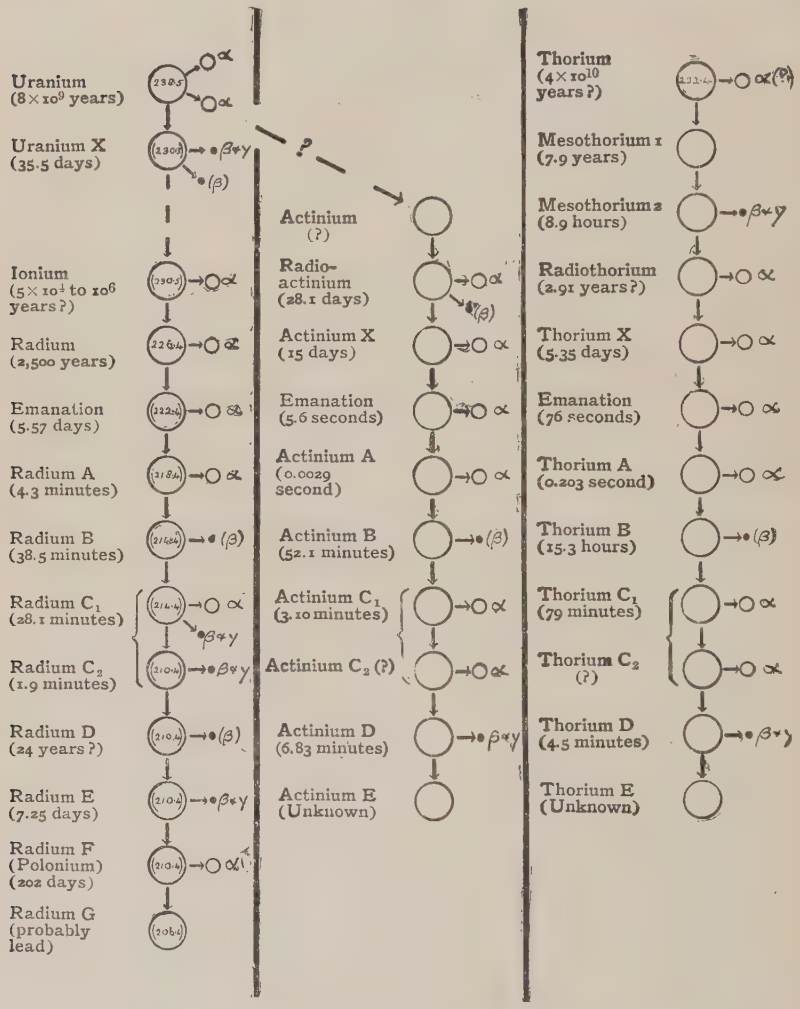
[48] H. Geiger, *Phil. Mag.*, 1911, [vi], **22**, 201; *A.*, ii, 683.
[49] *Ann. Report*, 1906, 343. [50] Giesel, *Ber.*, 1903, **36**, 342; *A.*, 1903, ii, 193.
[51] E. Rutherford and H. Geiger, *Phil. Mag.*, 1911, [vi], **22**, 621; *A.*, ii, 955.

The periods of these two new α-ray-giving products have been accurately determined by a rotating disk method.[52] On the periphery of the metal disk presses a sector-shaped box with its edges lined with velvet and containing a source of either of the emanations. Inside the box a wire gauge is positively charged, repelling the product of the emanation on to the disk. Two sector-shaped ionisation chambers are mounted opposite other portions of the periphery, the faces opposite the rotating disk being covered with goldbeater's skin and aluminium leaf. From the relative ionisation in these two chambers, their angular distance apart and the speed of the disk, the period of the products can be determined. That from thorium proved to have a half-period of 0·145 second, and that from actinium 0·002 second.

These short-lived α-ray-giving products, standing as they do intermediate between the emanation and the (β)-ray or almost rayless next product of the active deposit, both of which are much longer lived, are obviously in every respect analogous to radium-*A* in the radium active deposit. The half-period of radium-*A*, about three minutes, although short, is much longer than those of the new products, and radium-*A* has always been recognised as a separate member of the series. Hence it is necessary to alter the nomenclature of the thorium and actinium active deposit series, and to give to the new substances the names actinium-*A* and thorium-*A*. The *A*-members in each of the three cases are now short-lived, and give α-rays. What have before been termed thorium-*A* and actinium-*A*, are now called thorium-*B* and actinium-*B*. These are in every respect analogous to radium-*B*. In each case the *B*-member is the longest-lived of the active deposit group, and gives only relatively insignificant (β)-radiation. The next members of the two series hitherto termed thorium (*B* and *C*) and actinium-*B* are now, therefore, termed thorium-C_1 and -C_2 and actinium-*C*, or -C_1 and -C_2. The evidence of two products in the thorium series is indirect, and confined to the two sets of α-rays emitted. In the case of actinium, the evidence is of similar nature but less definite. These products are thus analogous to radium-*C*. The *C*-members give α-rays, and are shorter lived than the *B*-members. Now an unfortunate difference occurs. The next or *D*-members of the active deposits of actinium and thorium are relatively short-lived, and the powerful β- and γ-rays of the active deposits come entirely from these *D*-members. In the radium active deposit, radium-*C* has been shown to be complex (p. 286). What is probably a branch product, called radium-C_2, gives only β- and γ-rays, and no α-rays. The α-ray-giving radium-*C*, unlike the other *C*-members, seems to give β- and γ-rays

[52] H. G. J. Moseley and K. Fajans, *Phil. Mag.*, 1911, [vi], 22, 629; *A.*, ii, 956.

also. Hence the next member, radium-*D*, which is the well known long-lived member, giving only insignificant (β)-rays, and often called radio-lead, is not analogous to actinium-*D* and thorium-*D*, but to their products, the stable, unknown, ultimate members of



these series. The changes of nomenclature, whilst of necessity very confusing, result on the whole in a much better system, in which the close analogies between the successive members of the three active deposits are brought out, the analogous members now having analogous designations, with the exception just noted of radium-*D*.

Above has been reproduced, by the kind permission of the

publishers, Messrs. Longmans, Green and Co., a chart from a recent book,[53] showing the disintegration series of the radio-elements so far as they are at present known. The periods given are the periods of average life, which are 1·45 times the half-period.

Multiple Disintegration.

Radium-C_1 *and* -C_2.—The idea that in addition to the main disintegration series branch or subsidiary series may occur, has long been considered to be the best means of explaining the formation of the actinium series. Actinium, since it always occurs in constant relative amount in the uranium minerals, must be looked upon as derived in some way from uranium, but its small relative quantity in comparison with the other members of the uranium series precludes the possibility that it can form an intermediate member of the main series.[54] The first experimental evidence of the formation of branch series was obtained during the year in a study of radium-*C*. The complexity of this member, and the existence of a subsequent product, termed radium-C_2, of half-period between 1 and 2·5 minutes, and separable by recoil methods, was already known.[55] In the new work[56] much larger quantities of radium were available. The feature about the recoil of radium-C_2 from the active deposit is the extraordinarily minute amount of the product so obtained, which indicates that it is formed in a β-ray rather than in an α-ray change. From this, erroneously, it had been concluded that radium-C_1 gives the β- and γ-rays, and that radium-C_2 gives the α-rays. However, radium-C_2, the half-period of which was found as the result of some fifty determinations to be 1·38 minutes, gives no α-rays, but only β-rays identical in penetrating power to those furnished by radium-*C* as a whole. Neither does radium-C_2 give rise to any α-ray-giving product on disintegration. A small quantity of ordinary radium-*C*, giving α-, β-, and γ-rays, and having the 19·5 minutes half-period, is, it is true, always recoiled with the radium-C_2, but it was proved to be present from the start. The product of radium-C_2 remains unknown. Hence, on the one hand, the α-rays must come from radium-C_1, and on the other, radium-C_2 cannot be the product of the α-ray change of radium-C_1, for, if it were so, a considerable fraction of the whole product should be recoiled. The β-activity of the recoil product is, however, only about 1/20,000th of that of the source. What, then, is the product

[53] "Monographs of Inorganic and Physical Chemistry," edited by Professor Alexander Findlay. "The Chemistry of the Radio-Elements," by Frederick Soddy. Longmans, Green and Co. 1911.

[54] *Ann. Report*, 1909, 260. [55] *Ibid.*, 1909, 248.

[56] K. Fajans, *Physikal. Zeitsch.*, 1911, **12**, 369; *A.*, ii, 569.

of the α-ray change of radium-*C*, a considerable fraction of which must recoil at the moment of its formation? Experiments proved that it is radium-*D*. Plates left on to collect the recoil product of radium-*C* whilst that substance completely decayed, were inactive at first, but developed α- and β-activity at the rate characteristic of the formation of radium-*F* and -*E* from radium-*D*. In this way it was found that about 25 per cent. of the total number of radium-*D* atoms formed were received by recoil on the plate. It follows that radium-*D* must be the direct product of the α-ray change of radium-C_1, and that therefore radium-C_2 cannot be an intermediate product in the main radium-polonium disintegration series. The proportion of the number of radium-C_1 atoms changing respectively into radium-C_2 and into radium-*D*, the kind of radiation accompanying the two modes of disintegration, and the nature of the product of radium-C_2 remain unanswered problems. It appears that radium-C_2 accounts for only a small part of the total β-radiation of radium-*C*. Possibly the product of radium-C_2 may prove to be actinium. In addition, it must be remembered that it is very unlikely that the α-rays of radium-C_1 come directly from radium-C_1, for the half-period of this substance is 19·5 minutes, whereas the period calculated from the range of the α-particle is a millionth of a second (p. 275).

The ice having, as it were, been broken by the foregoing research, it is natural that the same explanation of an atom being capable of disintegration in more than one mode should be used as a way of escape in other cases, not amenable to other explanation, but the evidence in these other cases is still far from complete.

Uranium-Y.—Differences have been observed in uranium-*X* preparations separated from carefully purified uranium salts in different ways. In some there is a larger proportion of the very feebly penetrating (β)-radiation than in others, and this excess decayed with the half-period of 1·5 days, whereas the half-period of uranium-*X*, and of the decay of the main penetrating β-rays, and also of the γ-rays, is 24·6 days. The name uranium-*Y* was given to the product of half-period 1·5 days. Uranium-*X*, separated from a uranium solution by precipitating barium sulphate therein, behaved normally; but when separated by adding an iron salt, and precipitating it by boiling, there was obtained a rapid initial fall in the decay curve for the uncovered preparation, but a normal decay curve when the measurements are taken through 0·01 cm. or more of aluminium. A very feeble α-radiation, decaying also, so far as could be determined, with the 1·5 days half-period, was also detected by the scintillation method. The feebleness of this α-radiation in comparison with the (β)-radiation is unusual. It was never

found possible to separate more than a very small amount of the new product, and the recovery curve of uranium from which uranium-*X* had been separated was always normal, and showed no evidence of existence of the new member. In absence of other explanation, it is considered that uranium-*X* and -*Y* may be simultaneous products of uranium, the uranium-*Y* being formed in relatively minute quantity.[57] The question arises whether the short-period member, uranium-*Y*, does not give rise to some of the β-rays moving with velocity approaching closely that of light (p. 279), for an experiment has been recorded in which a rapid diminution of this part of the β-radiation of a preparation of uranium-*X* took place during the first few hours, the γ-radiation remaining constant over the same interval.[58]

Thorium-C_1 *and* -C_2.—The evidence for the complexity of this substance depends on the two sets of α-rays of different range emitted.[59] Since one of these sets of α-rays has the longest known range, it has always been surmised that the change in which it resulted was of immeasurably short period, so that the product producing it could not be separately distinguished from its parent. Were this so, thorium-*C*, like the emanations of actinium and thorium, should give rise to double scintillations. An examination,[60] however, disproved this. The intervals between the successive scintillations are such as, in the main, accord with the theory of probability, and it is therefore not possible that thorium-C_2 can be a direct, very-short-lived product of thorium-C_1.

The failure of recoil methods to separate thorium-C_2 proves that neither can it be produced from thorium-C_1 through an intermediate parent. The conclusion has been drawn that thorium-C_1 and the parent of thorium-C_2 (the period of which, as calculated from the range of its α-particle, can only be immeasurably short and of the order of 10^{-12} second) are the simultaneous products of thorium-*B*. In support of this it has been found that of the two sets of α-rays given by the *C*-member, 64·6 per cent. have the longer range, and 35·4 per cent. the shorter range, whereas if the two products were successive the numbers of α-rays ought to be the same for each. This ratio does not alter as the active material decays. The fact also that the total α-radiation of pure thorium-*C* decays exponentially, shows that, on this hypothesis, the periods of thorium-C_1 and the parent of thorium-C_2 must be identical. Also we have seen (p. 282) that there is some reason to believe that both members give the same product, thorium-*D*. The nearness of the

[57] G. N. Antonoff, *Phil. Mag.*, 1911, [vi], **22**, 419; *A.*, ii, 844.

[58] Soddy, *ibid.*, 1909, [vi], **18**, 862; *A.*, 1910, ii, 10.

[59] *Ann. Report*, 1906, 342.

[60] E. Marsden and T. Barratt, *Proc. London Phys. Soc.*, 1911, **24**, i, 50.

ratio of the numbers of the two sets of α-particles to 2 : 1 is suggestive, however, for if thorium-C_2 gave two α-particles per atom disintegrating to only one given by thorium-C_1, the products still might be successive. This, however, involves the view that the emanation and thorium-A both give three α-particles per atom disintegrating. Obviously experiment and reasoning have for the time being reached a position of stale-mate.

In the case of the actinium active deposit also, no double scintillations were observed, but here the evidence in favour of two products is altogether less definite.

It has been pointed out that the rule that in the radium series one α-particle is expelled per atom disintegrating, where the disintegration is accompanied by α-rays, does not appear to be followed in the thorium and actinium series.[61] The recent advances in our knowledge of the two latter series do much to remove this difference. Taking into account the new short-lived A-products of the active deposits, and assuming the simultaneous production of the C_1- and C_2-products just discussed, the facts are consistent with the view that the emanations, the A-products, and the C-products may all give only one α-particle per atom disintegrating, and so in this respect fall into line with the radium series.

The Periods of the Longer-lived Radio-elements.

Actinium, concerning the period of which no data whatever have been available, if the progress of time confirms some recent observations, may prove to be far from a long-lived radio-element.[62] In a research which included also the variation with time of the activity of uranium, radium, and radium-D, it was found that the activity of an old preparation of actinium, as measured by the β-rays, had decreased by about 10 per cent. in the last three years, a rate of decay which, if continued, indicates a period of average life of the order of only thirty years. The individual measurements were inexplicably irregular, as compared with those of the other substances, and the means of a large number of observations were compared. Another explanation also suggests itself from the almost complete analogy between the actinium and thorium series. The β-activity of thorium compounds freshly prepared from minerals decays, as is well known, for two years to a minimum, owing to the decay of the radiothorium separated always quantitatively with the thorium, in the absence of its immediate parent, mesothorium, which is separated quantitatively from the thorium. The period of radioactinium, however, is too short to explain the observed

[61] *Ann. Report*, 1909, 236.

[62] Mme. Curie, *Le Radium*, 1911, **8**, 353; *A.*, ii, 1047.

decay, and, in addition, radioactinium, being separable from actinium, is in this respect not analogous to radiothorium. To account for the decay, two new members between actinium and radioactinium, the first separable, the second non-separable, from the actinium, must be postulated. The alternative explanation, that actinium has a period of only thirty years, carries with it the corollary that its reproduction should be easily detectable, and this has so far not been observed.

No variation of activity was observed in the α-radiation of uranium oxide. The β-rays of radium showed a steady increase of almost 2·5 per cent. per year, due doubtless to the gradual formation of radium-*D*. Both the α- and β-rays of radium-*D*, three years after preparation, showed for the next two years a regular decay corresponding with a period of average life of about 25 years.

The period the least known, next to that of actinium, is the period of ionium. An upper and lower limit of 30,000 and a million years, respectively, have been assigned.[63] The first is arrived at from the failure, so far, to detect with certainty the production of radium from uranium, on the assumption that ionium is the only long-lived intermediate product. The latter follows from the weight of "thorium oxide" separated by Auer von Welsbach from the residues of some tons of pitchblende,[64] on the assumption that the "thorium oxide" was in reality pure "ionium oxide," and that all the ionium present in the mineral was actually separated. To the extent the first assumption is wrong the period would be reduced, and to the extent the second is wrong it would be increased. The range of the α-rays of ionium, as already indicated, corresponds with the period of nearly a million years (p. 275).

General Properties and Methods of Preparation of the Radio-elements.

It is often essential to be able to separate a radio-element without appreciable quantities of inactive matter, as in the separation of the active deposits from the emanations, so that the radiations shall be emitted without first having had to pass through absorbing material. Much useful practical information of two of the common methods, the electrolysis of solutions, and the deposition of the active material by immersing its solution in a less "noble" metal, has recently been published.[65] With regard to the first method, a silver cathode and platinum anode connected to a 220 volt circuit

[63] F. Soddy, *Le Radium*, 1910, **7**, 297. [64] *Ann. Report*, 1910, 276.
[65] L. Meitner, *Physikal. Zeitsch.*, 1911, **12**, 1094; *A.*, 1912, ii, 10.

through a 25 c.p. carbon lamp, and placed about 1 mm. apart in the rapidly boiling solution of the active substance, the volume of which is kept as small as possible, are the conditions recommended. From slightly acid solutions of the respective active deposits, electrolysis separates radium-*B* and -*C* together, *E* and *F* together, thorium-*B* sometimes with a little thorium-*C*, and actinium-*B* with some actinium-*C* and -*D*. Before electrolysis, if desired, radium-*C*, thorium-*C*, and actinium-*C* may all be quantitatively separated in the pure state by immersing in the solutions a nickel plate, whilst radium-*F* may be removed similarly by bismuth.

The *D*-products of thorium and actinium giving β- and γ-rays are most easily prepared by recoil methods. Actinium-*D*, it should be noted, has been given somewhat too low a period. A new determination, from 50 curves, gave the mean value for the half-period of 4·71 minutes.[66]

In the preparation of mesothorium-2, the mesothorium solution is precipitated by ammonia after adding a trace of iron. After daily precipitations for a few days, the radiothorium and thorium-*X* are got rid of, and there is then obtained only mesothorium-2 and a little thorium-*B* with the iron. Electrolysis of the acid solution with a platinum cathode first separates the iron and thorium-*B*. The mesothorium-2 can then be deposited electrolytically on a silver cathode from the boiling, nearly neutralised solution.

A method which is claimed to be of general utility in the separation of radioactive materials, and is recommended in lieu of fractional crystallisation, is the adsorption of the radioactive substance by shaking the solution with metasilicic acid gel, prepared by the hydrolysis of dilute vapour of silicon tetrachloride and the dialysis of the solution obtained. The silica is removed, after filtration and drying, by volatilisation with hydrofluoric acid.[67] The method is novel and contrary to general experience, in that the silicic acid, separating on evaporation from solutions of radioactive minerals in acid, adsorb hardly any radioactive matter. No special conditions are laid down for the operation of the method, and such a preferential adsorption of radioactive substances by silica is very open to question.

It is notable that of the ten radio-elements of longest period, only three, uranium, actinium, and polonium, have a distinct chemical nature different from that of any other known element, and in the case of the first the evidence that it consists of a non-separable pair of elements differing in atomic weight by 4 units has been frequently alluded to. Thorium is chemically non-

[66] A. F. Kovarik, *Physikal. Zeitsch.*, 1911, **12**, 83; *A.*, ii, 173.
[67] E. Ebler and M. Fellner, *Ber.*, 1911, **44**, 2332; *A.*, ii, 957.

separable from ionium, radiothorium, and uranium-X; mesothorium-1 is non-separable from radium, a statement which applies also to the two substances of shorter period, thorium-X and actinium-X; radium-D or radio-lead is non-separable from lead. These statements are not at all, as might be supposed, merely negative expressions of failure due to the difficulties of investigation. The statement, for example, that mesothorium-1 is non-separable from radium completely describes the chemistry of that substance so far as it is known, and indicates, for example, that it is differentiated most definitely from every one of the whole of the rest of the common elements. In addition, the three emanations are chemically non-separable from the other members of the zero group of the Periodic Table. The other radioactive substances known are, with two or three exceptions, members of the three active deposit groups. The ease with which these groups are isolated, unmixed with inactive matter, from the volatile emanations possibly accounts for the fact that none of them are known to resemble known elements. It must be remembered, however, that they represent in the Periodic System the transition, through the non-valent emanations, from the electropositive elements, at the beginning of one period, to the electronegative elements at the end of the last period. Von Lerch's well-known rule that the successive members of the active deposit groups become progressively more "noble" in their electrochemical behaviour, at least until the C-members are reached, is significant in showing that this transition is not abrupt, but through a succession of well-defined, if very unstable, forms. In the periodic classification, the three VIIIth groups occur only in the middle of the long periods, and not between the ends of these periods (halogen elements) and the beginning of the next (argon gases). Hence the active deposit groups, which in their electrochemical behaviour resemble the noble metals, although they would fall in the VIIIth group in the usual classification, are related to them very much, for example, as the elements, zinc, cadmium, and mercury, are related to the alkaline earth elements.

The chemical nature of the radio-elements is thus becoming fairly completely known, in spite of the fact that in no field is more entirely untrustworthy experimental work published.

Uranium Minerals.

To avoid the errors and the laborious operations of the solution method of estimating minute quantities of radium in rocks and minerals, a fusion method has been devised.[68] An electrically heated platinum crucible is covered with a quartz bell jar made

[68] J. Joly, *Phil. Mag.*, 1911, [vi], **22**, 134; *A.*, ii, 685.

air-tight by standing in an annulus on the bed plate, filled with mercury, so that the gas expelled in the fusion of the mineral with fusion mixture or borax is collected and can be tested in the electroscope after the fusion. The method is rapid, and gives, as a rule, a much higher radium content than the solution method. With acidic rocks, the fusion is accompanied by vigorous effervescence, which assists the escape of emanation. The same result may be attained in the case of basic rocks if boric acid is added to the mixture before fusion. Very small quantities of reagents are necessary, and there is greater certainty against contamination during the determination than in the usual method, which is open to grave uncertainties owing to there never being a complete guarantee that some of the radium has not been precipitated out in the non-emanating condition.[69]

A number of papers have been published on the question whether the ratio of radium to uranium in minerals is a completely constant quantity, even when palpable exceptions, such as autunite, are excluded. It will be recalled that one investigation in which the radium was separated chemically, prior to estimation by the emanation method, indicated that the older the mineral, the higher was the radium ratio.[70]

In the continuation of this work twenty-one minerals were examined which, on the whole, bore out the former conclusion. The ratio was highest for minerals from Cornwall, and for Cornish pitchblende exceeded that for the Joachimsthal pitchblende by about 20 per cent.[71] In another research confined principally to an examination of the ratio in pitchblendes and thorianites, similar variations were observed for certain specimens, but the specimens least liable to have been contaminated with radium before examination gave a ratio constant within the limits of error.[72] In a further research, in which the minerals were dissolved in hot concentrated sulphuric acid to liberate the emanation, the ratio for thorianite and East African pitchblende was the same as for Joachimsthal pitchblende within the limit of error.[73] The low ratio for the autunite was accounted for by the loose formation of the mineral and the action of percolating water. The same explanation was held to cover the absence of helium and lead. A determination of the ionium-radium ratio in the minerals showed

[69] A. S. Eve and D. McIntosh, *Trans. Roy. Soc., Canada*, 1910, [iii], **4**, III, 67 ; *A.*, ii, 841.

[70] *Ann. Report*, 1909, 260.

[71] Mlle. E. Gleditsch, *Le Radium*, 1911, **8**, 256 ; *A.*, ii, 845.

[72] R. Pirret and F. Soddy, *Phil. Mag.*, 1911, [vi], **21**, 652 ; *A.*, ii, 454.

[73] W. Marckwald and A. S. Russell, *Ber.*, 1911, **44**, 771 ; *Jahrb. Radioaktiv. Elektronik*, 1911, **8**, 457 ; *A.*, ii, 360.

that the ratio for autunite and carnotite, although somewhat lower than for Joachimsthal pitchblende, is sufficiently near the normal to disprove views advanced previously with regard to these minerals.[74] The question is in rather an unsettled state. The action of percolating water in removing radium from autunite beds is known from the case of the radiferous pyromorphite of the Issy l'Eveque district.[75] It is, however, difficult to believe that the action of percolating water can have anything to do with the absence of lead, helium, and the variability of the radium ratio in the massive, almost perfect, unweathered crystals of autunite encountered in the Portuguese deposits, or that this material has more than a transitional existence in geological time. Probably recrystallisation of the material is in actual active operation at the present day, it being dissolved out by water charged with carbon dioxide in one place and deposited in another. That these compact crystals have been in existence indefinitely, and that the lead, for example, as formed throughout the mass of the crystal, is removed by percolating water leaving the crystal undissolved and even unweathered, is more difficult to suppose than that the mineral itself is being continually dissolved and re-deposited. With regard to the whole question, leaving out of account all disturbing elements, there remains some doubt as to the absolute constancy of the uranium-radium ratio in minerals, regardless of their age, as the disintegration theory, in its present form, requires, but whether the variations observed have a theoretical significance is still an open question.

The determination of geological age from the uranium-lead ratio has been carried out for a series of thorite-bearing nepheline-syenites, probably of lower Devonian age, found in the Christiania district. The district—a depressed area of 4000 square miles—was chosen because of its isolation from the surrounding rocks by faults on every side. The minerals examined—thorite, zircon, apatite, and sphene—contain much larger proportions of uranium than the surrounding magma, so that the segregation of the mineral from the magma furnishes a definite starting point from which the accumulation of disintegration products commences. The ratio of lead to uranium in 15 of these minerals was tolerably constant, increasing somewhat from 0·041 to 0·068 as the quantity of uranium decreased. Possibly this increase is due to the initial presence of some lead in the minerals. The results show a ratio sufficiently near constancy to be very striking. From the mean value the age of the formation was deduced to be 370 million years.[76]

[74] *Ann. Report*, 1910, 263. [75] *Ibid.*, 1909, 260.
[76] A. Holmes, *Proc. Roy. Soc.*, 1911, A, **85**, 248; *A.*, ii, 570.

The Radium Series.

Radium.—A new determination of the atomic weight of radium, in which a gram of radium chloride was available, gave the number 225·95 (Ag = 107·88, Cl = 35·457), which is nearly half a unit lower than the accepted value. After this atomic weight had been reached, 50 crystallisations of the hydrochloric acid solution, and 13 precipitations with alcohol, caused no further change in the atomic weight. The chloride was melted in hydrogen chloride before weighing. In one series the chloride was precipitated as silver chloride and weighed, the amount of silver chloride in the washings being estimated by the nephelometer. In another series the amount of silver necessary for the complete precipitation of the chlorine in a weighed amount of the chloride was found.[77]

A new determination of the arc and spark spectra of radium confirms, for the most part, previous determinations. In both spectra two of the radium lines, namely, 3814·6 and 4682·4, were visible in a preparation containing only 0·001 per cent. of radium. The line 5017·9 was ascribed to barium, and 6439·1 to calcium. In the weaker preparations lines due to scandium and yttrium were observed, and in the spark spectrum an unidentified line, 3993·25, was seen, strongest in the weakest preparation, and fading as fractionation proceeded.[78]

From a consideration of a large number of the properties, such as heat of solution and formation of the halogen salts, sulphates, selenates, hydrides, and carbides, so far as they are known, the affinity of oxides for oxygen, the solubility of the fluorides, hydroxides, and carbonates of the metals of the alkali and alkaline-earth families, these elements were found to form a regular series, in which the properties augment or diminish regularly in the order: calcium, lithium, strontium, barium, sodium, potassium, rubidium, cæsium. In this series radium enters between barium and sodium, and many of its physical and chemical constants, still undetermined, have been calculated from this analogy.[79]

Radium Emanation.—Two careful series of measurements of the solubility of radium emanation in various liquids at various temperatures have been caried out, in which, after the gas and liquid phases have come into equilibrium, they have been separated and left four hours, after which time the γ-radiation furnishes a convenient measure of the amount of emanation secured by each

[77] O. Hönigschmid, *K. Akad. Wiss. Wien, Sitzung.*, 19th Oct., 1911.

[78] F. Exner and E. Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, June, 1911, **120**, IIa.

[79] R. de Forcrand, *Compt. rend.*, 1911, **152**, 66; *A.*, ii, 172.

phase.[80] The solubility in water is given as 0·51 at 0°, 0·39 at 9°, 0·303 at 14°, 0·285 at 18°, and 0·153 at 40°. The temperature-coefficient is thus very important. Glycerol (0·21 at 18°) is the only liquid found dissolving less emanation than water, the other organic liquids all absorbing much more strongly than water. Carbon disulphide absorbs 80 times, and aniline 13 times more than water, the other solubilities determined being intermediate. Henry's law was obeyed exactly, which is of interest in view of the excessively minute partial pressures involved. The volatilisation temperature of radium emanation has also been re-investigated by a new method.[81]

Discussion has taken place with regard to the origin of the carbon dioxide from thorium solutions submitted to the action of radium emanation.[82] Thorium nitrate, specially purified to avoid as far as possible organic impurities, and which gave carbon dioxide under the action of the emanation, gave it also when treated with potassium permanganate. On the other hand, an account of the methods employed in the preparation of the thorium nitrate used in the original experiments and the precautions taken to secure contamination from carbon has been published, but so far no actual analysis of this thorium preparation for carbon has been recorded.

Radium-D.—A novel but unsuccessful attempt has been made to put into evidence the metallic nature of radium-*D* by depositing it from the radium emanation in a capillary tube of very small volume provided with two electrodes and measuring the resistance between the electrodes as the change of the emanation occurred.[83] Attempts were made to make good contact between the platinum electrodes and the tube by silvering the tube except over the area between the electrodes, but the silvering became transparent under the action of the emanation. Traces of deposits of brilliantly metallic lustre by reflected light were observed in some of the experiments, as in similar ones by other observers. The deposits, however did not form uniformly, but in restricted areas, and the resistance of the tube in all cases remained above a megohm as when initially prepared. They also disappeared like the silver deposits in the course of time.

The Thorium Series.

Mesothorium-1.—Technically prepared mesothorium is obtained from monazite sand containing about 0·3 per cent. of uranium and

[80] E. Ramstedt, *Le Radium*, 1911, **8**, 253; *A.*, ii, 842. R. W. Boyle, *Phil. Mag*, 1911, [vi], **22**, 840; *A.*, 1912, ii, 10.

[81] R. W. Boyle, *Phil. Mag.*, 1911, [vi], **21**, 722; *A.*, ii, 569.

[82] H. Herschfinkel, *Compt. rend.*, 1911, **153**, 255; *Le Radium*, 1911, **8**, 417; *A.*, ii, 843. Sir W. Ramsay, *Compt. rend.*, 1911, **153**, 373; *A.*, ii, 843.

[83] L. Kolowrat, *Le Radium*, 1911, **8**, 401.

4 to 5 per cent. of thorium oxide, and of its penetrating rays 75 per cent. are due to mesothorium, and 25 per cent. to radium. The maximum of activity, due to the regeneration of radiothorium, is reached in 3·2 years. It may be fractionated until its penetrating rays are initially about four times as intense as those from pure radium salts, and from the ratio of the periods of the two substances it is then estimated to contain 1 per cent. by weight of mesothorium and 99 per cent. of radium.[84] Thus the determination of the spectrum, for example, of mesothorium seems to be bound up with the possibility of finding a thorium mineral sufficiently free from radium. Some monazite sands appear to contain far less uranium than that given above, so that the problem may be capable of solution.[85]

Radiothorium.—The half-period assigned to this member is two years, but some recent measurements have put a much lower value —a few months only—on the period.[86] This is, however, contrary to the general experience of those who have measured the decay of the activity of technical preparations directly.

Thorium Emanation.—The molecular weight of the thorium emanation, determined by a modification of Bunsen's effusion method,[87] gave a result in the neighbourhood of 200, the extreme values being 210 and 194. Part of the uncertainty arises from the period of the emanation not being very exactly known, any error in the period introducing a five-fold greater error into the calculation of the molecular weight.[88]

Chemical Actions of the Rays of Radium.

The decomposition of hydrogen peroxide by the rays of radium has been much studied.[89] The natural rate of decomposition is increased both in paraffined and not paraffined vessels, and there is in some cases an after-working, due probably to the decomposition of the glass by the rays and the production of new substances capable of producing catalytic action. The rate of decomposition increases with rise of temperature, very much the same as in photochemical reactions, and much less rapidly than the rate of the unassisted decomposition.

[84] O. Hahn, *Chem. Zeit.*, 1911, **35**, 845; *A.*, ii, 845.

[85] Compare Haitinger and Peters, *Sitzungsber. K. Akad. Wiss. Wien*, July, 1911, **120**, IIa.

[86] Miss M. S. Leslie, *Le Radium*, 1911, **8**, 356; *A.*, ii, 1048.

[87] Compare *Ann. Report*, 1910, 278.

[88] Miss M. S. Leslie, *Compt. rend.*, 1911, **153**, 328; *A.*, ii, 843.

[89] K. von Körösy, *Pflüger's Archiv*, 1910, **137**, 123; *A.*, ii, 9. A. Kailan, *Monatsh.*, 1911, **32**, 1019; *A*, 1912, ii, 10.

The volume changes of ammonia under the action of the rays from an uncovered radium salt have been studied.[90] After an initial contraction for five weeks, which is ascribed to the presence of air, steady expansion occurred for a year. With the apparatus filled with undried air, a regular contraction occurred, which went on for four months, whilst with dry nitrogen a similar contraction for one month took place. The decomposition of water by the α- and β-rays of radium has been re-investigated.[91] The β-rays from 1 curie of emanation give 6·486 c.c. of mixed gas during complete change, whereas when the emanation is dissolved in water, so that there is only the liquid phase present, 136·66 c.c. result. The chemical action is ascribed to the charges on the rays rather than to mechanical consequences of the collisions between the molecules and the radiant particles.

Radium bromide, sealed up with perfectly dry hydrogen and oxygen, causes no combination, but the ionisation of ordinary air by the rays of radium is not affected by perfect drying. Radium bromide brings about the complete mutual decomposition of hydrogen sulphide and sulphur dioxide in a few hours, the whole of the water and sulphur formed condensing on the radium salt. It has been suggested that the power of the ions to condense liquid water drops, in which the chemical action occurs, may explain the influence of moisture on chemical change. For it was found that 10 milligrams of radium bromide, exposed at the ordinary temperature for two days to an atmosphere saturated at 0°, collected 1·5 milligrams of liquid water.[92] That this is an effect of ions apart from the lowering of the vapour pressure by the dissolved salt was not, however, proved. The colours produced in various minerals and other substances by comparatively large quantities of radium have also been investigated.[93]

It seems worth while calling attention here to one point in regard to the chemical action of the rays of radium on air which seems to have been overlooked, and which forced itself on the attention of the writer many years ago. Nitrous oxide is produced in comparatively large quantity, for example, if air containing emanation is stored over mercury. For this reason it is impossible to obtain the emanation pure by condensation with liquid air, if previously, as, for example, by leakage, it has become mixed with air. As the emanation rapidly destroys the lubrication of stopcocks, the only way to avoid leakage is by the use of a mercury seal between the radium solution and the pump. Quite frequently, in

[90] E. P. Perman, *Trans.*, 1911, **99**, 132.
[91] F. L. Usher, *Jahrb. Radioaktiv. Elektronik.*, 1911, **8**, 323; *A.*, 1912, ii, 6.
[92] H. B. Baker, *Royal Institution Lecture*, delivered March 11, 1911; *A.*, ii, 244.
[93] C. Doelter and H. Sirk, *Monatsh.*, 1910, **31**, 1057; *A.*, ii, 171.

reading the literature, unrecognised examples of this formation of nitrous oxide from air are met with, so that attention may be directed to it. No doubt the radium emanation in the air is one of the agents in the formation of combined nitrogen, heretofore attributed to electrical discharges.

Radioactivity of the Earth and Atmosphere.

The papers in this section, which are very numerous, can only be briefly referred to. An extensive survey of the Leinster granite, which covers an area of 600 square miles, showed a mean content of radium of $1{\cdot}7 \times 10^{-12}$ gram, and of thorium of $7{\cdot}1 \times 10^{-6}$ gram, per gram of rock. On the whole, the proportion between the two elements was wonderfully uniform, but the three samples richest in radium did not contain thorium.[94] Some rocks from the Antarctic region of S. Victorialand were very similar in their content of radium and thorium to those just described.[95] Something of the nature of a constant ratio, about 2×10^{-7}, between the elements seems, as a rule, to occur. Except for the granites, which have usually a high radium content, and of which a disproportionate number have been investigated, the mean content of radium in sedimentary as well as igneous rocks appears similar, at about $1{\cdot}4 \times 10^{-12}$ gram per gram.[96] An investigation of the α- and β-activity of rocks has given results not always in agreement with determinations by the emanation method, as though other unrecognised radio-elements than radium and thorium might be present.[97]

With regard to the amount of radium emanation in the air it is notable that in the middle of the Atlantic Ocean the quantity does not appear to be greatly different from that near the coast.[98] Several series of experiments have been done on the escape of emanation from the soil into the air.[99] It has been established that a very rapid escape of emanation occurs, much influenced by the hygrometric condition of the soil and by the fluctuations of the barometer, and that this is probably the only source of the emanation found in the air. The amount of radium emanation in the air drawn up from underground is many thousand times greater than that present

[94] A. L. Fletcher, *Phil. Mag.*, 1911, [vi], **20**, 102 ; *A.*, ii, 89.
[95] A. L. Fletcher, *ibid.*, **21**, 770 ; *A.*, ii, 570.
[96] E. H. Büchner, *Proc. K. Akad. Wetensch., Amsterdam*, 1911, **13**, 818 ; *A.*, ii, 243.
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in the atmosphere. A mean value of 80×10^{-12} curie per cubic metre of the atmosphere has been deduced. Less found at Tokyo by indirect methods may be capable of another explanation.[1] With regard to the penetrating rays from the earth, although the opinion that this is accounted for by the known amounts of radioactive matter in the earth's crust is the prevalent one, the opinion has also been expressed that part is independent of this origin and persists over the surface of the sea, and that this part is subject to notable rapid oscillations in magnitude.[2] The absorption of these penetrating rays by the air should be easily detectable even at an altitude of only 100 metres, whilst at an altitude of 1000 metres their effect should be negligible.[3] Some experiments from the Clock Tower of the Toronto City Hall, 64 metres high, bear out these calculations.[4]

F. Soddy.

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